



Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Isotopic studies of the Upper and Middle Rio Grande. Part 2 – Salt loads and human impacts in south New Mexico and west Texas

Anna Szyrkiewicz^{a,b,*}, David M. Borrok^{b,c}, Girisha K. Ganjgunte^d, Grzegorz Skrzypek^e, Lin Ma^b, Michael S. Rearick^f, George B. Perkins^f

^a University of Tennessee, Earth and Planetary Sciences, 1412 Circle Drive, Knoxville, TN, USA

^b University of Texas at El Paso, Geological Sciences, 500 W. University Ave., El Paso, TX, USA

^c School of Geosciences, University of Louisiana at Lafayette, 611 McKinley St., P.O. Box 44650, Lafayette, LA 70504, USA

^d Texas AgriLife Research Center, Texas A&M University System, El Paso, TX, USA

^e West Australian Biogeochemistry Centre, School of Plant Biology, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

^f EES-14 Earth System Observations, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

ARTICLE INFO

Article history:

Received 7 October 2014

Received in revised form 28 March 2015

Accepted 25 May 2015

Available online xxxx

Keywords:

Salinity

Arid

Rio Grande

Human impact

Isotopes

ABSTRACT

Increasing groundwater and soil salinity is a threat to the land and water resources in arid regions. Global warming will likely increase salinity of dryland river systems. In order to characterize salt loading into the semi-arid portion of the Rio Grande in south New Mexico and west Texas, we sampled seasonally (2009–2011) the river, agricultural drains, and saline groundwater. In addition to major element chemistry, these samples were analyzed for sulfur and oxygen isotope compositions ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) of dissolved SO_4 and in some cases for nitrogen and oxygen isotope compositions ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) of dissolved NO_3 . Uranium isotopes ($^{234}\text{U}/^{238}\text{U}$ activity ratio) were also measured for selected samples. The natural inflow of basinal brines/groundwater ($\delta^{34}\text{S}$ of +8 to +11‰) in the semi-arid Rio Grande study area was minor in the investigated seasons and could not be detected by the $\delta^{34}\text{S}$ mass balance. However, we did find localized increases of $\delta^{34}\text{S}$ (+2 to +5‰) in the Rio Grande that were attributable to salt loads from the intersections of agricultural drains with the water table of a natural salt flat and associated evaporative brine ($\delta^{34}\text{S}$ of +12‰) in the shallow subsurface. In the areas, with higher water use for land irrigation, the $\delta^{34}\text{S}$ of the river and drain water was relatively consistent (from ~0 to +2‰) compared to the $\delta^{18}\text{O}$ (from ~+2 to +6‰). Most likely, this resulted from application of S-rich fertilizers (e.g., ammonium sulfates, elemental S, sulfuric acid) with low $\delta^{34}\text{S}$ (–2 to +4‰) and high $\delta^{18}\text{O}$ (+9 to +16‰). Additionally, we observed considerably lower $\delta^{18}\text{O}$ (SO_4) in the Rio Grande and agricultural drains (<7‰) compared to geologic and anthropogenic SO_4 sources (+9 to +16‰), which likely resulted from microbial recycling of SO_4 in soil of the irrigated land related to assimilatory sulfate reduction. Shallow recharge to the Rio Grande was also inferred from the lower $^{234}\text{U}/^{238}\text{U}$ activity ratios (1.62 to 1.88) compared to deeper groundwater (2.54 to 2.64) and the distinctive $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of nitrates (+5 to +25‰ and –5 to +15‰, respectively) typical for septic effluents that are undergoing denitrification. Agricultural practices during flood irrigation intensify evaporation of the Rio Grande surface water and considerably increase water salinity. This process is also important in the evolution of water chemistry toward a Na– SO_4 –Cl-rich composition and precipitation of secondary calcite in soil profiles.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The Rio Grande is the major source of water for flood irrigation in southern New Mexico and west Texas (Ellis et al., 1993). The Rio Grande surface water is diverted to cultivated fields through a complex system of canals and some of this water is subsequently returned to the river via a network of agricultural drains and/or shallow groundwater recharge (Fig. 1). High water use is particularly concentrated in the semi-arid

portions of the middle Rio Grande from central/south New Mexico below Elephant Butte Dam through far west Texas (Fig. 2). At present, high salt loads within the riverine hydrologic system greatly decrease the water quality and the crop productivity (e.g., Piccioni et al., 2000; Ganjgunte et al., 2011; Simpson et al., 2014).

One of the biggest uncertainties related to salt loads in the Rio Grande is their poorly-defined sources and how agricultural practices contribute to the increasing salinity. Currently, there are large disagreements among scientists, stakeholders, and government agencies on the extent to which the salinity of the Rio Grande is controlled by natural versus anthropogenic processes. Flows of deeply-derived, saline fluids through a complex network of faults and upwelling of brines at the

* Corresponding author.

E-mail address: aszyrk@utk.edu (A. Szyrkiewicz).

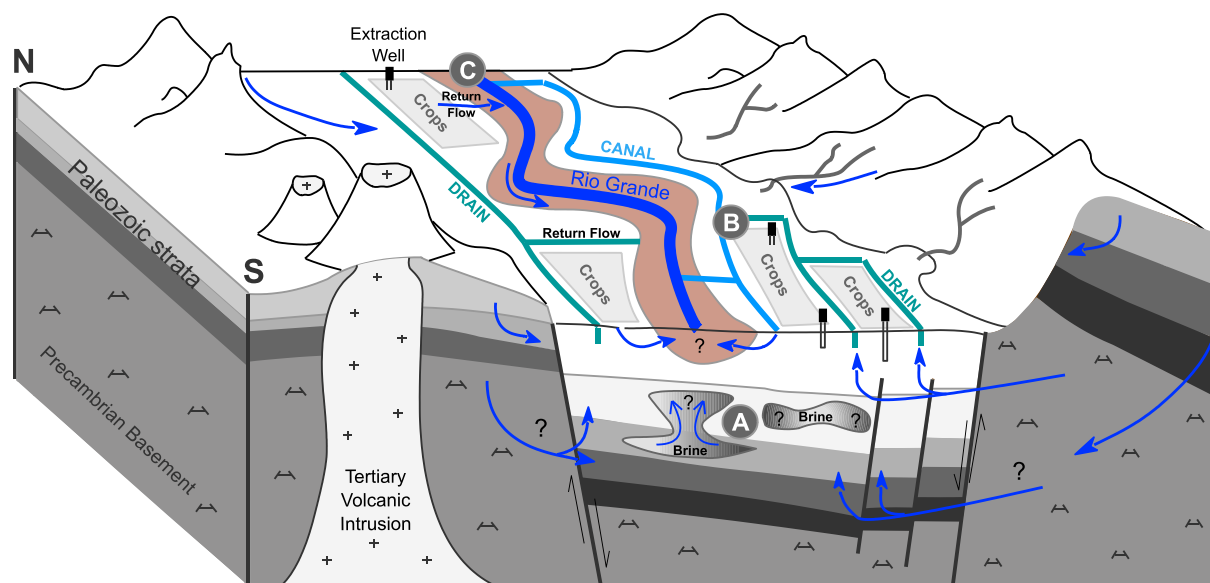


Fig. 1. A conceptual model of the hydrological cycle and anthropogenic impacts in the semi-arid portion of the Rio Grande watershed in our study area. Blue arrows indicate directions of water flow. The previously suggested major sources of salinity are as follows (e.g., Hogan et al., 2007; Szyrkiewicz et al., 2011): (A) natural flow of brines, saline groundwater, and/or deep saline fluids; (B) anthropogenic salts from flood irrigation; (C) geologic salts from weathering of crystalline/volcanic and sedimentary rocks in upstream Rio Grande. (For figure in color, the reader is referred to the web version of this article.)

termini of geologic sub-basins (Process A in Fig. 1) are believed to be major natural sources of salinity in the Rio Grande watershed (Phillips et al., 2003; Hogan et al., 2007; Williams et al., 2013). In addition,

enhanced evapotranspiration rates (Phillips et al., 2003) coupled with flood irrigation and the application of fertilizers are also thought to be important anthropogenic factors (Processes B–C in Fig. 1) for increased

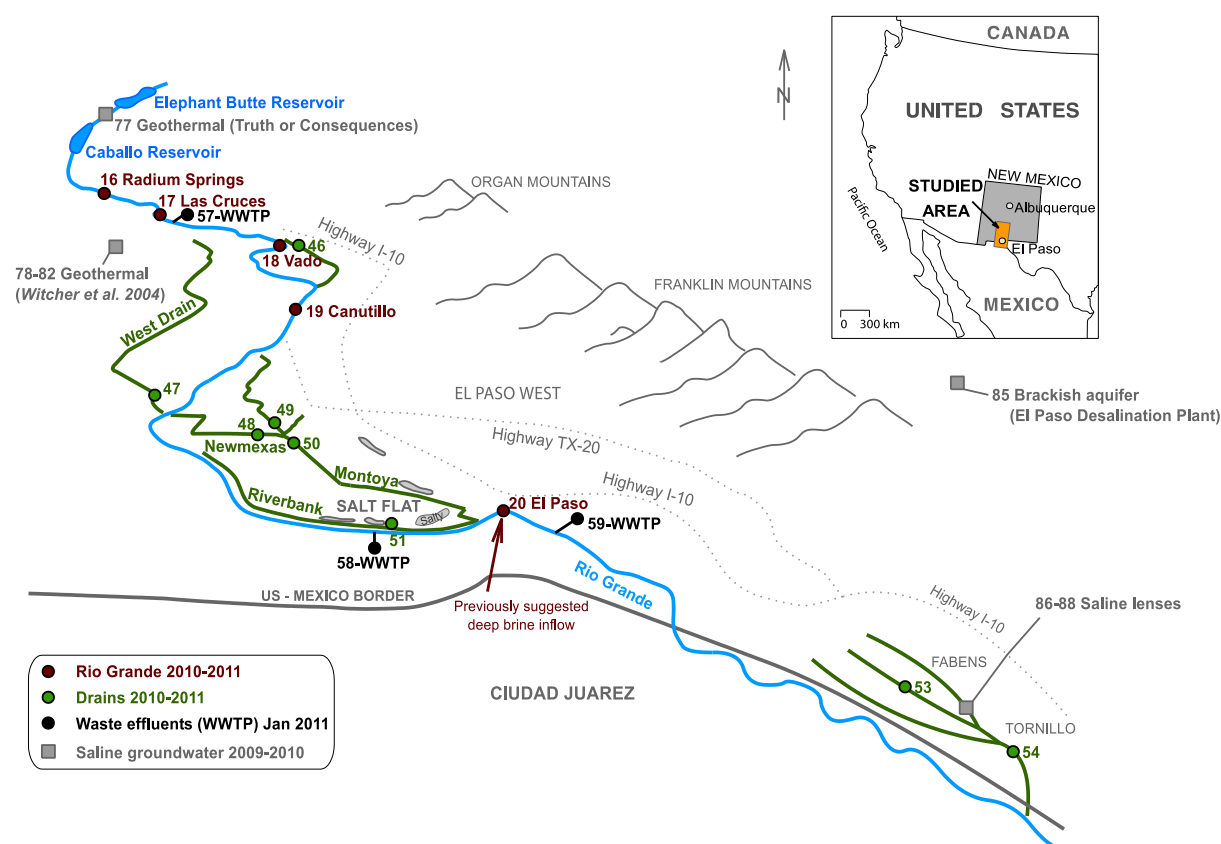


Fig. 2. Simplified sketch (not to scale) showing the location of the water sampling points selected for seasonal observations (2010–2011) in the Mesilla (Locs. 16–20) and Hueco–Bolson basins (Locs. 53–54). The gray elongated areas around the Montoya drain indicate salt accumulation in the salt flat located in west El Paso. The distance between Radium Springs (#16) and El Paso (#20) is ~90 km, and between El Paso (#20) and Tornillo (#54) is ~65 km. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

salt loads in the Rio Grande (Wilcox, 1957; Trock et al., 1978; Szyrkiewicz et al., 2011).

The transition to a more arid climate, followed by increasing evaporation rates and decreasing stream flows that are predicted for the American Southwest (e.g., Gutzler and Robbins, 2010), will further degrade the already overstressed water resources in the Rio Grande watershed. Moreover, population centers that utilize water in this area of the Rio Grande valley like Las Cruces, New Mexico, El Paso, Texas, and Juárez, Mexico (Fig. 2) continue to grow. Questions are arising about how to meet increasing water demand in a system plagued by dwindling surface water and high salt loads. Therefore, the problem of delineating the sources of salt loading in the Rio Grande is becoming critical, as this is the first step in understanding how to address these challenges. In this study, we report new geochemical data (elemental, and sulfur (S), oxygen (O), nitrogen (N), and uranium (U) isotopes) for surface water and groundwater samples collected seasonally between 2009 and 2011. We use these data to evaluate the relative importance of different sources of salts linked to natural processes and anthropogenic activities. Furthermore, we discuss the respective roles of these processes and how they might affect future management practices designed to prevent further salinization of water resources.

2. Environmental setting

The Rio Grande flows through a series of alluvial-fill basins formed by half grabens that were formed during the Rio Grande rift ~30 Ma ago during an episode of widespread extension of the western United States (Keller and Baldrige, 1999). These basins are filled with alluvial, fluvial, playa, and lacustrine sediments derived from erosion of adjacent Precambrian crystalline and Paleozoic sedimentary bedrock highlands and range in depth from less than 30 m to 4000 m (Keller and Cather, 1994). The majority of recharge to the Rio Grande occurs in the spring from snowmelt in the headwater region in southwest Colorado and in the high mountain areas of north New Mexico (Ellis et al., 1993). Further, smaller recharge to the Rio Grande occurs during summer monsoon. Average annual precipitation delivered to the semi-arid stretch of the Rio Grande is less than 254 mm (Ellis et al., 1993) and decreases southward reaching less than 203 mm in El Paso, Texas.

In the studied semi-arid area of south New Mexico and West Texas (Fig. 2), the Rio Grande is regulated by the Elephant Butte and Caballo reservoirs in central/south New Mexico. In addition to its widespread agricultural use, the Rio Grande surface water of the studied area is partly used by the cities of Las Cruces, New Mexico and El Paso, Texas, to supplement aquifer groundwater for municipal purposes. The flow volume and the water quality of the Rio Grande decrease downstream (e.g., Hogan et al., 2007; Szyrkiewicz et al., 2011). Elevated salt concentrations and low flows preclude the use of Rio Grande water for agricultural and municipal purposes during the non-irrigation season (October through February) when water is being stored in the Elephant Butte reservoir. In many locations, the Rio Grande disappears entirely from the surface. During these times, agricultural drains and municipal waste effluents from the cities of Las Cruces and El Paso become the major tributaries to the Rio Grande below Elephant Butte Dam. Conversely, in the irrigation season (March through September) stream flows increase (and salt concentrations decrease) when water is released for irrigation downstream of Elephant Butte and Caballo reservoirs.

The irrigation system in the Rio Grande basin is a complex network of shallow irrigation canals (above the water table) combined with deeply cut channels (drains) that are incised to the groundwater table. The canals move irrigation water to individual agricultural fields, while the drains alleviate salt build up during flood irrigation. Eventually, these drains flow back to the Rio Grande (e.g., Anderholm, 2002).

This paper is mainly focused on the stretch of the Rio Grande valley in the Mesilla basin, between Radium Springs, New Mexico and west El Paso, Texas (Fig. 2). In El Paso, the Rio Grande becomes an international border of the United States with Mexico. Various security measures

on the border precluded us from some surface water sampling in this area in 2009–2011. Nevertheless, we expanded our sampling campaigns to the agricultural drains located further east and south of El Paso in Fabens and Tornillo, Texas (Fig. 2). These drains are major flow contributors to the Rio Grande along the international border, thus, their water quality is reflective of that of the Rio Grande.

3. Methods

3.1. Field sampling

Between June of 2010 and March of 2011 surface water samples were collected monthly at locations 16 through 20, and from four agricultural (Locs. 46–48, 50) and three drains in west El Paso (Locs. 49–51; Fig. 2). The drains in west El Paso comprise a combination of flows from agricultural drains and storm drains. In the studied Rio Grande stretch (~100 km long) intense agriculture practices take place in the Rio Grande valley. Additionally, seasonal water samples were collected in two agricultural drains ~60 km south of El Paso, Texas, in Fabens and Tornillo, Texas (Locs. 53–54; Fig. 2). Waste water effluents were also collected from Las Cruces (Loc. 57), New Mexico, and west El Paso, Texas (Locs. 58–59).

In addition to surface water samples in the Rio Grande, drains, and waste effluents, we sampled several locations thought to be representative of the saline groundwater endmembers previously indicated as important in increasing the salinity of the Rio Grande (e.g., Witcher et al., 2004; Hibbs and Merino, 2006; Hogan et al., 2007). These included saline geothermal water from an artesian well (41 °C) in Truth or Consequences, south New Mexico (Loc. 77), brackish groundwater from a municipal well (27 °C) used by the El Paso Desalination Plant, Texas (Loc. 85), and saline packets (lenses) of groundwater underlying the agricultural fields near Fabens, Texas (Locs. 86–88).

In all locations, the sampled water was filtered in the field with a 0.45 µm nylon filter into two 125 mL plastic bottles. One bottle was acidified with 16 drops of high-purity concentrated HNO₃ for cation and uranium (U) isotope analyses. The second portion was left untreated for anion analysis. Unfiltered surface water samples were collected in 0.25–1.0 L plastic bottles that were rinsed three times with the sample water prior to collection. These were processed and analyzed for the S and O isotope compositions of dissolved sulfate (SO₄). Temperature, pH, and conductivity were measured in situ for surface water and groundwater samples using an Orion portable meter (Thermo Scientific 3 Star Multimeter). Alkalinity was measured in the field using a LaMotte titration kit (LaMotte Company, Maryland, USA) with analytical error of ± 4 mg/L.

3.2. Fertilizers

Liquid and solid samples of fertilizers were obtained from the Helena Fertilizer company/distributor located in Tornillo, Texas (Loc. 54; Fig. 2). Additionally, the samples of fertilizers containing pure gypsum and elemental S were obtained from a local farmer living in the same area. The chemical analyses of the Helena fertilizers were done by Actlabs Life Sciences in Ancaster, Ontario, Canada. For S and O isotope analyses, the fertilizers were dissolved in DI-water. Afterward, the dissolved SO₄ was precipitated as BaSO₄ by reaction with 10–20 mL of 10% BaCl₂ and analyzed for δ³⁴S and δ¹⁸O as described below. The fertilizers containing gypsum and elemental S were analyzed for S isotopes as mineral phases without prior laboratory treatment.

3.3. Chemical analyses

The concentrations of major cations in all water samples were measured using a Perkin Elmer 5300 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) at the University of Texas at El Paso. Samples (diluted with de ionized water to 1:10, 1:100 or 1:1000)

were analyzed using multi-element atomic adsorption standards (diluted from 10.00 mg/L stock solutions) and the U.S. Geological Survey standard reference water samples were used as external checks of precision and accuracy. The concentrations of anions in all water samples were measured using EPA method 300 on a Dionex DX-600 equipped with conductivity detection at Los Alamos National Laboratory. An AG14 guard column and AS14 separator column were used in conjunction with a Dionex ASRS 300 2 mm suppressor to separate the anion species and reduce the background conductivity. The mobile phase composition was 3.5 mM Na₂CO₃ and 1.0 mM NaHCO₃. Calibration standards were prepared from a stock solution of anions purchased from SPEX Certiprep®. Samples were diluted and re-run in cases where elemental concentrations were outside the initial calibration range. Because of required dilution, particularly for the samples of river/drain/well water showing higher salinity (conductivities in the range of 1–5 mS/cm), the analytical uncertainty was considerably higher (10 to 20%) as compared to the water samples with lower ion concentrations that did not require as much dilution. The concentrations of NO₃ and PO₄ were measured using a Hach DR 2800 spectrophotometer accompanied by TNT835 and PhosVer® kits.

3.4. S and O isotope analysis

All collected surface water and groundwater samples were analyzed for the S and O isotope compositions of their dissolved SO₄ ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$, respectively). After arrival in the laboratory, raw water samples were filtered, acidified with HCl, and dissolved SO₄ was precipitated as BaSO₄ by reaction with 10–20 mL of 10% BaCl₂. Prior to drying, the BaSO₄ precipitate was rinsed several times with DI-water. The $\delta^{34}\text{S}$ of BaSO₄ was determined using an EA1110 elemental analyzer coupled to a Finnigan Mat 252 isotope ratio mass spectrometer via a ConFlo II split interface in the Stable Isotope Research Facility at Indiana University. S isotopic data are reported with respect to VCDT (Vienna Cañon Diablo Troilite). Analytical reproducibility was better than 0.3‰ based on sample duplicates. Given that the water samples were not filtered in situ in the field, we subsequently repeated precipitation of BaSO₄ on several samples stored in the refrigerator (4 °C) for 3–4 months. Consequently, the measured $\delta^{34}\text{S}$ of BaSO₄ was within the analytical error of $\pm 0.3\%$ compared to the BaSO₄ of water samples processed a few hours after sampling.

The $\delta^{18}\text{O}$ of BaSO₄ was analyzed in a continuous flow system using a high temperature conversion elemental analyzer (TC/EA) coupled with a Delta XL Mass Spectrometer (Thermo-Fisher Scientific, Bremen, Germany) at the University of Western Australia. BaSO₄ was thermally decomposed in a highly-reductive environment and $\delta^{18}\text{O}$ was analyzed in the CO gas yielded, which was carried in helium stream. The raw δ -values were normalized using a multipoint normalization technique (Skrzypek and Sadler, 2011; Skrzypek, 2013) based on international standards (IAEA601, IAEA602, SO-5, SO-6 and NBS127) provided by International Atomic Energy Agency from Vienna (IAEA). Analytical reproducibility was better than 0.3‰ based on duplicates.

3.5. N and O isotope analysis

Water samples were analyzed for aqueous nitrate nitrogen and oxygen isotope ratios using a modified version of the microbial denitrification technique described by Casciotti et al. (2002) and Sigman et al. (2001) using *Pseudomonas aureofaciens* (ATCC 13985). Stable nitrogen and oxygen isotope compositions were measured for N₂O in continuous flow mode using a GV Instruments Isoprime isotope ratio mass spectrometer (GV Instruments, Manchester, UK) in the Los Alamos National Laboratory. Analytical linearity was monitored and corrected for by analyzing standards after every five samples. An analysis blank, consisting of the identical tryptic soy broth and NaOH solution used for samples was used in the blank correction procedure. All stable isotope ratios are reported in the standard δ -notation as the per mil deviation (‰)

relative to Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{18}\text{O}$ and atmospheric N₂ for $\delta^{15}\text{N}$. A calibration curve for $\delta^{15}\text{N}$ was constructed using analyses of IAEA-NO-3 and USGS32 ($\delta^{15}\text{N}_{\text{air}} = +4.7$ and $+180\%$ vs. atmospheric N₂, respectively). $\delta^{18}\text{O}$ values were calibrated using analyses of IAEA-NO-3 and USGS34 ($\delta^{18}\text{O} = +25.6\%$ and -30.9% vs. VSMOW, respectively). Within each analytical run, the precision on five replicates of standard solution IAEA-NO-3 was consistently $<0.25\%$ for $\delta^{15}\text{N}$ and $<0.50\%$ for $\delta^{18}\text{O}$.

3.6. Uranium series isotope analysis

We selected several surface water samples from the semi-arid portion of the Rio Grande (Locs. 9, 10, 11, 13, 15, 16, 19, 20) and drains (Locs. 49, 50, 54) sampled in 2009–2010 for U series isotope analysis. The site locations and general characterization of these samples have been presented in Szyrkiewicz et al. (2015). Additionally, three representative samples of groundwater with elevated salinity (Locs. 75, 77, 86) and two fertilizer samples (U ~ 200 ppm) were analyzed. About 30 g of water sample and ~100 mg of fertilizer sample were weighed and spiked with an artificial ²³³U tracer. Afterward, the fertilizer samples were fully dissolved using ~2 mL concentrated ultrapure HNO₃. All sample solutions were evaporated on hotplates. Afterward, the evaporated precipitate was dissolved in 1 mL 7.5 N HNO₃ and the U was separated from solution and purified using conventional cation exchange chromatography (Pelt et al., 2008; Ma et al., 2010). The U isotopic ratios (²³⁴U/²³⁸U and ²³³U/²³⁸U) were measured on a Nu-plasma MC-ICP-MS using ~25 ng of U per sample. The measured (²³³U/²³⁸U) ratios allow for calculation of U concentrations in the original samples (isotope dilution method). The standard-sample bracketing technique (with NBL 145B as the U bracketing solution) was used to correct for mass discrimination and drafting of ion counter/faraday cup gains during the measurements. Uncertainties on U isotope ratios and U concentration were ~1%. USGS rock reference standard (BCR-2) was analyzed along with samples for data quality assurance. The measured values for BCR-2 are: (²³⁴U/²³⁸U) = 1.003 ± 0.001 and U concentration = 1.686 ± 0.010 ppm (n = 2); both are in agreement with the reference values: BCR-2 (²³⁴U/²³⁸U) = 1.000 and U concentration = 1.69 ± 0.02 ppm (Sims et al., 2008). The U procedural blanks were ~20 pg.

3.7. Mass flux calculations

Using a combination of online gauging station data collected from the U.S. Geological Survey, the U.S. International Boundary and Water Commission, and the El Paso County Water Improvement District No. 1, we were able to reconstruct the volumetric flow rates for the Rio Grande at Canutillo (Loc. 19) and at west El Paso (Loc. 20), and for the agricultural drain in Tornillo (Loc. 53). Using these volumetric flow rates we were able to calculate elemental mass loads (Suppl. Table. 1) by multiplying the stream water concentrations (in mg/L) by the flow rates (in L/s) and then converting the units to metric tons/day.

3.8. Chemical modeling

Saturation indices (SIs) for the formation of calcite, gypsum, thenardite and halite were calculated for the water samples using the geochemical modeling program, PHREEQC™ (Parkhurst and Appelo, 1999). Saturation indices are reported as the log of the ion activity product (IAP) divided by the equilibrium solubility product (K_{sp}) for a given mineral phase. Using this convention, SI = 0 indicates equilibrium with respect to a mineral phase, and SI > 0 and SI < 0 represent oversaturation and undersaturation with, respectively.

4. Results

All in situ, chemical and isotope measurements for the studied Rio Grande, drain, groundwater, and waste water effluent samples are listed

Table 1
Isotope and chemical compositions of fertilizers in the semi-arid portion of Rio Grande, south New Mexico and west Texas.

Fertilizer	Description	$\delta^{34}\text{S}$ [‰]	$\delta^{18}\text{O}$ [‰]	SO_4 [%]	S [%]	Ca [%]	K [%]	Mg [%]	Na [%]	P [%]	Source
Helena 12-0-0	Brown granules (ammonium iron sulfate)	4.1	10.1	>60	>20	0.01	0.03	<0.01	0.04	0.009	New data - this study
Corton 21-0-0	White granules (ammonium sulfate)	0.3	16.8	>60	>20	0.02	0.02	<0.01	0.02	0.155	New data - this study
Corton 0-0-22	Pinkish white granules	10.1	8.3	>60	>20	0.2	2.72	10.9	0.55	0.014	New data - this study
F-White	White granules (ammonium sulfate)	–2.1	10.4	73	24	<0.01	0.03	<0.01	0.01	0.005	Szyrkiewicz et al. (2011)
F-Brown	Brown granules (ammonium sulfate)	4.8	10.5	74	24	0.02	0.03	<0.01	0.02	0.005	Szyrkiewicz et al. (2011)
Helena 20-0-20	White-brown-red hard grains	4.3	na	48	16	0.06	5.13	0.17	0.1	0.017	New data - this study
Del City gypsum	White fine-grained gypsum	9.3	17.1	56	19	23	na	na	na	na	New data - this study
Elemental Sulfur	Yellow coarse-grained pellets	0.2	na	na	100	na	na	na	na	na	New data - this study
16-8-3-4	Sulfuric Acid (pH < 1)	1.5	9.3	42	14	0.13	5.6	0.49	0.27	12	Szyrkiewicz et al. (2011)
24-40	Sulfuric Acid (pH < 1)	1.6	9.1	61	20	0.34	0.11	0.35	0.39	11	Szyrkiewicz et al. (2011)
5-0-0-10	Sulfuric Acid (pH < 1)	1.4	9.6	94	31	0.11	0.05	0.007	0.30	0.1	Szyrkiewicz et al. (2011)
Helena 16-8-8	White-brown-red hard grains (5% Fe, 8% Gy)	5.1	na	25	8.4	2.11	3.58	0.29	0.27	4.73	New data - this study
Corton 11-52	Brown-white hard grains	0.1	16.2	8	2.51	1.81	0.33	0.55	0.31	15.2	New data - this study
Helena 14-14-14	White-brown-red hard grains	8.9	na	19	6.34	1.51	5.1	1.96	0.4	3.81	New data - this study
Corton 18-44-0	Brown hard grains	1.3	16.2	6	2.05	2.08	0.17	0.4	0.32	14.2	New data - this study
Helena 20-4-8	White-brown-red hard grains (5% Fe, 8% Gy)	13.6	16.9	14	4.73	2.53	4.97	1.06	0.27	2.59	New data - this study
Urea	White granules	bd	bd	0.15	0.05	0.03	0.04	0.01	0.02	0.013	New data - this study
	Average	4.0	12.5	40.0	19.4	2.3	1.9	1.5	0.2	4.3	
	Median	2.9	10.5	42.0	15.0	0.3	0.3	0.4	0.3	1.4	

in Supplementary Table 1. The chemical, S and O isotope measurements for the studied fertilizers are listed in Table 1.

4.1. Water chemistry

The electrical conductivity (EC) of the Rio Grande along the Mesilla basin (Locs. 16–20; Fig. 2) was lower in the irrigation season (~0.6–1.0 mS/cm) compared to the non-irrigation season (~1.3–3.5 mS/cm) (Suppl. Table. 1). Consequently, a similar pattern was observed for concentrations of major ions. In the irrigation season, lower concentrations were observed for SO_4 (~100–180 mg/L), Cl (~45–90 mg/L), Na (~60–115 mg/L), HCO_3 (~130–170 mg/L), Ca (~55–75 mg/L), K (~5–10 mg/L), and Mg (~10–15 mg/L) (Suppl. Table. 1). In contrast, higher concentrations were observed in the non-irrigation season for SO_4 (~200–650 mg/L), Cl (~150–520 mg/L), Na (~150–740 mg/L), HCO_3 (~180–300 mg/L), Ca (~100–150 mg/L), K (~10–25 mg/L), and Mg (~20–45 mg/L). The agricultural drains south of El Paso, Texas showed considerably higher EC and concentration units (EC 1.4–4.6 mS/cm, SO_4 250–750 mg/L, Cl 155–770 mg/L, HCO_3 190–340 mg/L, Na 180–600 mg/L, Ca 80–280 mg/L, Mg 20–60 mg/L, K 10–35 mg/L) compared to the agricultural/city drains in the Mesilla basin (EC 1.0–2.5 mS/cm, SO_4 140–530 mg/L, Cl 60–260 mg/L, HCO_3 150–355 mg/L, Na 130–325 mg/L, Ca 105–140 mg/L, Mg 10–35 mg/L, K 5–12 mg/L). Among all investigated drains, abnormally high EC was observed in the Montoya Drain (4.1 to 8.4 mS/cm), a city drain of west El Paso, Texas (Loc. 49). During the summer of 2010, the Montoya Drain contained up to ~1500 mg/L, ~1800 mg/L, and ~1350 mg/L of SO_4 , Cl and Na, respectively (Suppl. Table. 1). These concentrations measurably decreased to ~680 mg/L, ~600 mg/L, and ~680 mg/L, respectively, by the fall of 2010. Similarly high conductivity and concentrations of major ions were observed in the waste water effluents discharging to the Rio Grande in Las Cruces, New Mexico and west El Paso, Texas: EC 1.3–2.8 mS/cm, SO_4 120–530 mg/L, Cl 115–310 mg/L, HCO_3 140–300 mg/L, Na 175–365 mg/L, Ca 55–85 mg/L, Mg 10–45 mg/L, and K 12–32 mg/L (Suppl. Table 1).

The SO_4 versus Cl concentrations were positively correlated for the Rio Grande, drain, and waste effluent samples (Fig. 3A). A similar relationship was observed for the SO_4 versus HCO_3 concentrations (Fig. 3B). For comparison with our new chemical data (2010–2011), we call upon five previously measured geothermal groundwater samples (Nos. 78–82) from the Mesilla basin (Witcher et al., 2004) and two groundwater samples with elevated salinity (Nos. 75–76) collected by Szyrkiewicz et al. (2015) in Bosque del Apache, central New Mexico. In many cases, however, the saline and geothermal water samples plotted outside the positive trend of SO_4 versus Cl and HCO_3 (Fig. 3A, B).

The NO_3 concentrations of the Rio Grande samples usually varied over a range of <1 to 4 mg/L (Suppl. Table 1; Fig. 4A). However, important increases were observed locally in the Rio Grande at Vado, New Mexico (Loc. 18; ~27 to 46 mg/L) in November and December of 2010 (Fig. 4A) when there was constant stream flow present between Las Cruces and Vado, New Mexico. Conversely, in January and February of 2011 the NO_3 concentrations decreased to <1 mg/L in Vado (Fig. 4A) when the Rio Grande channel was mostly dry and only localized pools of ponding water were present along the river banks. The agricultural drains south of El Paso, Texas showed considerably higher NO_3 concentrations (4 to 13 mg/L) compared to the drains north of El Paso in the Mesilla basin (<1 to 2 mg/L) (Fig. 4B).

In most of the investigated locations, the concentrations of PO_4 were very low (<0.50 mg/L) (Suppl. Table 1). However, in some months the Rio Grande water showed slightly higher PO_4 concentrations in Vado, New Mexico (1.05 mg/L) and Canutillo (1.46 mg/L), and in El Paso, Texas (1.40 mg/L). Higher PO_4 concentrations were usually observed in the agricultural drains south of El Paso, Texas (0.15–1.77 mg/L) compared to the drains in Mesilla basin (0.06 to 0.45 mg/L) (Suppl. Table 1).

The NO_3 and PO_4 concentrations of the waste water effluent samples varied from ~10 to 50 mg/L and ~1 to 6 mg/L, respectively, except for

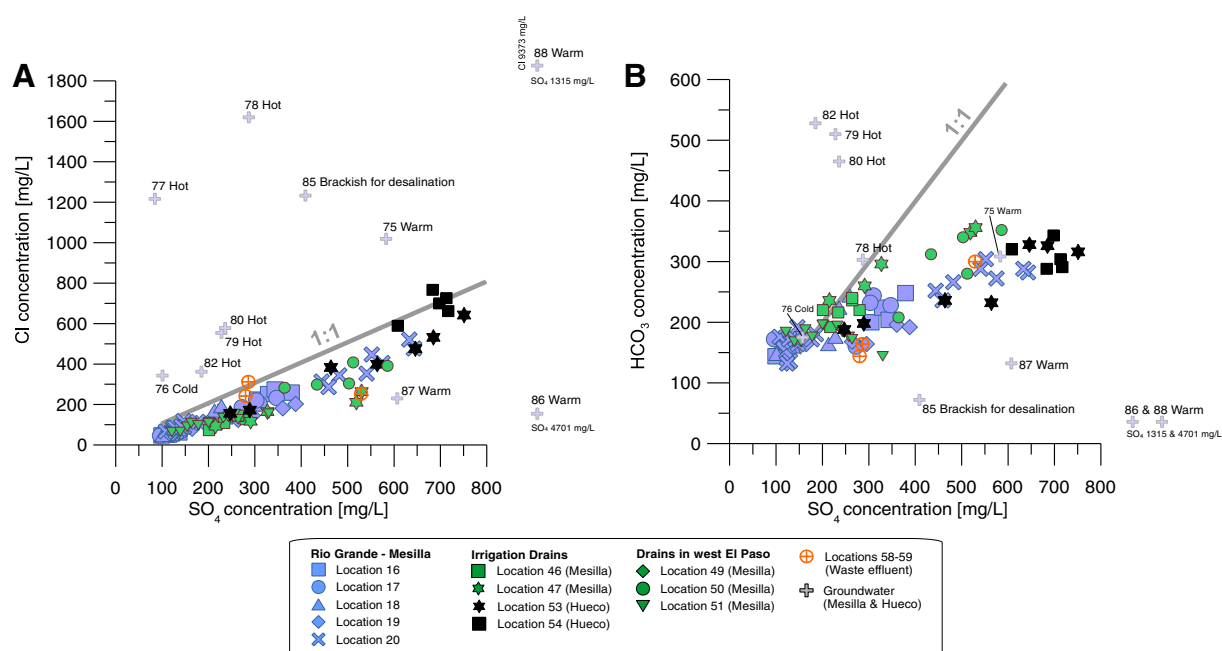


Fig. 3. Variations of SO_4 , Cl and HCO_3 concentrations in the analyzed water samples. Note that the concentrations of SO_4 and Cl in saline groundwater from Fabens (Loc. 86, $\text{SO}_4 = 4701$ mg/L and Cl = 150 mg/L; Loc. 88, $\text{SO}_4 = 1315$ mg/L and Cl = 9373 mg/L) plot outside the concentration ranges presented on both plots. Concentrations for Locs. 76–77 were adopted from Szyrkiewicz et al. (2015) and for Locs. 78–82 from Witcher et al. (2004). The gray lines (1:1) are example projections of evaporation trends. See Fig. 2 for the locations of sampling points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the waste effluent in Las Cruces, New Mexico (Loc. 57), which contained ~100 mg/L and ~16 mg/L of NO_3 and PO_4 on the date of our sampling, respectively (Suppl. Table 1).

4.2. N and O isotope compositions of NO_3

Randomly selected samples of the Rio Grande water (2009–2010), showed wide $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ variations with the lowest values upstream at Truth or Consequences (No. 77; +8.1‰ and –4.7‰, respectively) compared to higher values downstream at west El Paso (No. 20; +16.4 to +42.6‰ and +5.9 to +19.0‰, respectively). The $\delta^{15}\text{N}$ of agricultural drains south of El Paso (Locs. 53, 54) ranged from +17.5 to +24.2‰ and $\delta^{18}\text{O}$ from +5.4 to +8.7‰ (Fig. 4C).

4.3. S and O isotope compositions of SO_4

The $\delta^{34}\text{S}$ of SO_4 in the Rio Grande varied over a narrow range, from –0.6 to +2.5‰ (Fig. 5A). Only in west El Paso, Texas (Loc. 20) did the $\delta^{34}\text{S}$ show a distinctive increase from +1.4 to +5.0‰ in the non-irrigation seasons. The $\delta^{18}\text{O}$ of SO_4 in the Rio Grande varied from +4.6 to +8.1‰ (Fig. 5B).

The $\delta^{34}\text{S}$ of SO_4 in drains in the Mesilla basin (Locs. 46–51) varied over a greater range, from –0.7 to +5.1‰, compared to the agricultural drains south of El Paso (Locs. 53–54), from +1.2 to +2.8‰ (Fig. 6A). The Montoya Drain in west El Paso, Texas (Loc. 49), showed the highest $\delta^{34}\text{S}$, +6.1 to +7.2‰ (Fig. 6A). Conversely, the $\delta^{18}\text{O}$ of SO_4 in drains varied over a narrower range, from +5.0 to +8.1‰, with slight increases in the Montoya drain, from +8.0 to +9.4‰ (Fig. 6B).

The $\delta^{34}\text{S}$ of SO_4 in the saline groundwater endmembers varied from +7.9 to +10.5‰ (Fig. 7), while the $\delta^{34}\text{S}$ of the waste effluents in the studied cities varied from +3.8 to +7.1‰. The $\delta^{34}\text{S}$ of seventeen fertilizer samples varied from –2.1 to +13.6‰ (Fig. 7; Table 1). However, the average and median $\delta^{34}\text{S}$ were skewed toward the lighter end of this range, +4.0‰ and +2.8‰, respectively.

The $\delta^{18}\text{O}$ of groundwater SO_4 varied over a much wider range, from +3.5 to +11.2‰, with the lowest values in geothermal water at Truth or Consequences, New Mexico (Loc. 77) (Fig. 7). In contrast,

the $\delta^{18}\text{O}$ of waste effluent SO_4 varied over a smaller range (+2.2 to +3.0‰) (Fig. 7). The $\delta^{18}\text{O}$ of fertilizers had relatively high values of +8.3 to +17.1‰, with average and median values of +12.5‰ and +11.5‰ (Fig. 7; Table 1).

5. Discussion

5.1. Shallow versus deep groundwater inflows

Due to limited precipitation, enhanced agricultural activity, and the presence of populous urban centers in Las Cruces, New Mexico (Loc. 17), El Paso, Texas (Loc. 20), and Juárez, Mexico, large anthropogenic impacts on water availability and quality are observed in this portion of the Rio Grande (Fig. 2). Major use of the Rio Grande water in this region is for flood irrigation to grow pecans, chilies, cotton, alfalfa, and other minor crops that can tolerate elevated water salinity. In drier months (e.g., fall and winter), groundwater from the closely-connected alluvial aquifers of the Rio Grande Valley is used to supplement surface water for flood irrigation. While evapotranspiration is partly responsible for increasing salinity (e.g., Phillips et al., 2003), highly-saline geothermal water and deep basinal brines are locally important and have been previously proposed as major salinity sources to the semi-arid portion of the Rio Grande (Hibbs and Merino, 2006; Hogan et al., 2007). In following chapters, using new chemical and isotope results we discuss various salinity sources related to shallow and deep water flows and how they influence increasing salinity of the Rio Grande.

5.1.1. Evidence from major water chemistry

In addition to collecting water samples from the Rio Grande, we identified and collected samples from several salt-rich groundwater localities in order to characterize the end member geochemistries of these potential salt loading sources. Direct inflow of geothermal water to the Rio Grande, with high Cl and Na concentrations (~1870 mg/L and ~870 mg/L, respectively), occurs in Truth or Consequences (Loc. 77; Fig. 2), including from small spa resorts that use these waters (Szyrkiewicz et al., 2011). Additionally, groundwater may impact the Rio Grande in the Mesilla Valley as a result of pumping from

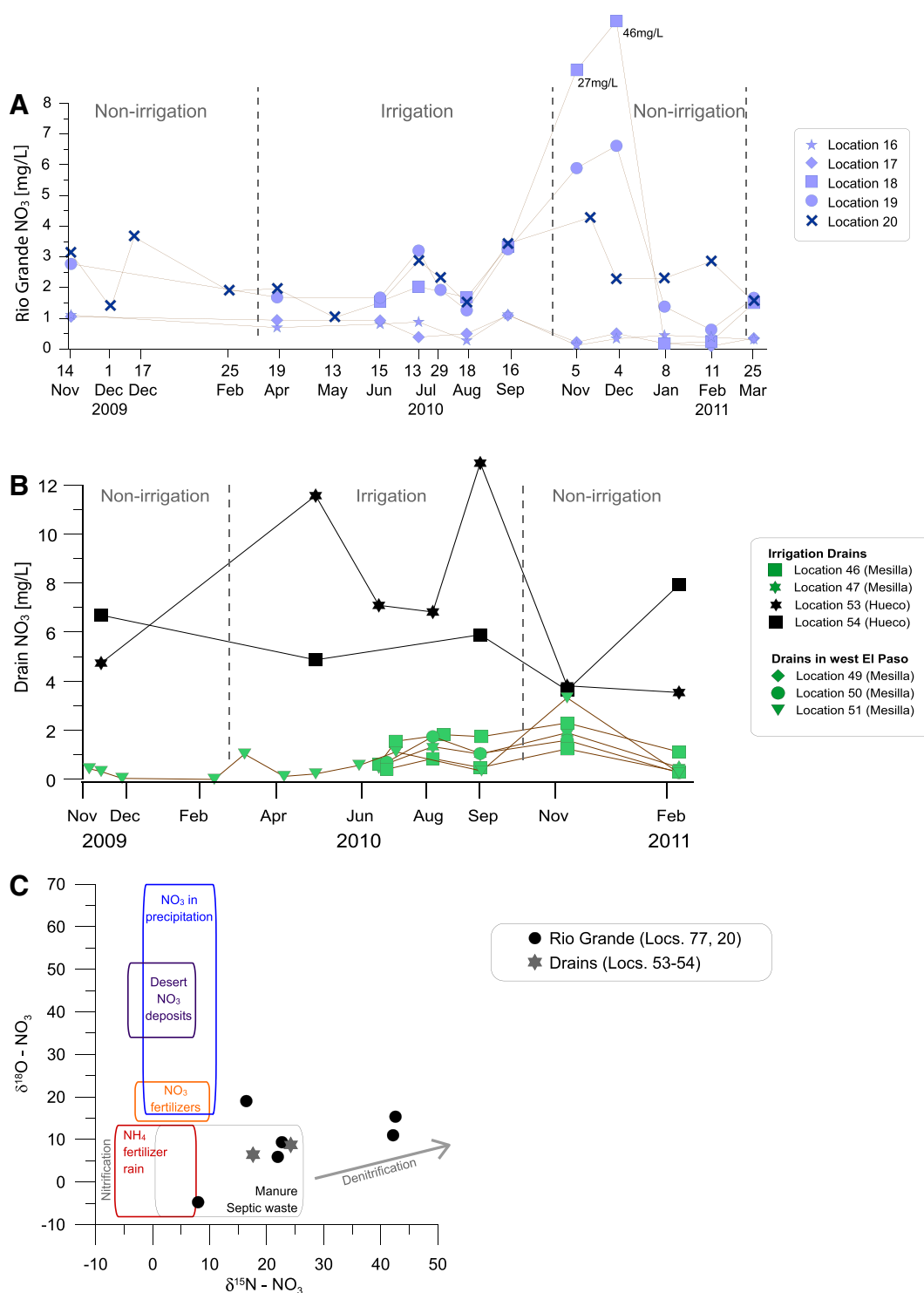


Fig. 4. Seasonal variation of NO_3 concentration in the Rio Grande in the Mesilla Valley (A) and in the sampled drains (B). The values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ are presented for a few locations (with highest concentrations in November 2009 and April 2010) in the Mesilla and Hueco–Bolson basins and compared to isotope compositions of various nitrate sources after Kendall (1998) (C). See Fig. 2 for the locations of sampling points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

domestic/agricultural wells in the Mesilla basin (Locs. 78–82). Saline groundwater lenses are also present at depths of ~30 to 200 m in the agricultural district near Fabens, Texas (Locs. 86–88). Finally, the brackish Hueco Bolson aquifer underlies much of eastern El Paso (Loc. 85) and Juarez, Mexico.

In most cases, the studied saline end members in Locations 75 through 82 and 85 through 87 (Fig. 2) showed different chemical compositions than the Rio Grande and plotted outside the major mixing

trend observed for the SO_4 versus Cl and HCO_3 for the Rio Grande and associated drains and waste effluents (Fig. 3). This implies that the contributions of salts from the saline end member groundwater compositions to the Rio Grande study area were negligible. For instance, geothermal and brackish water had high Cl concentrations (~500–1600 mg/L) but considerably lower SO_4 concentrations (~100–600 mg/L). In contrast, the saline lenses at Fabens had high SO_4 concentrations (~600–4700 mg/L) but low Cl concentrations (~200 mg/L);

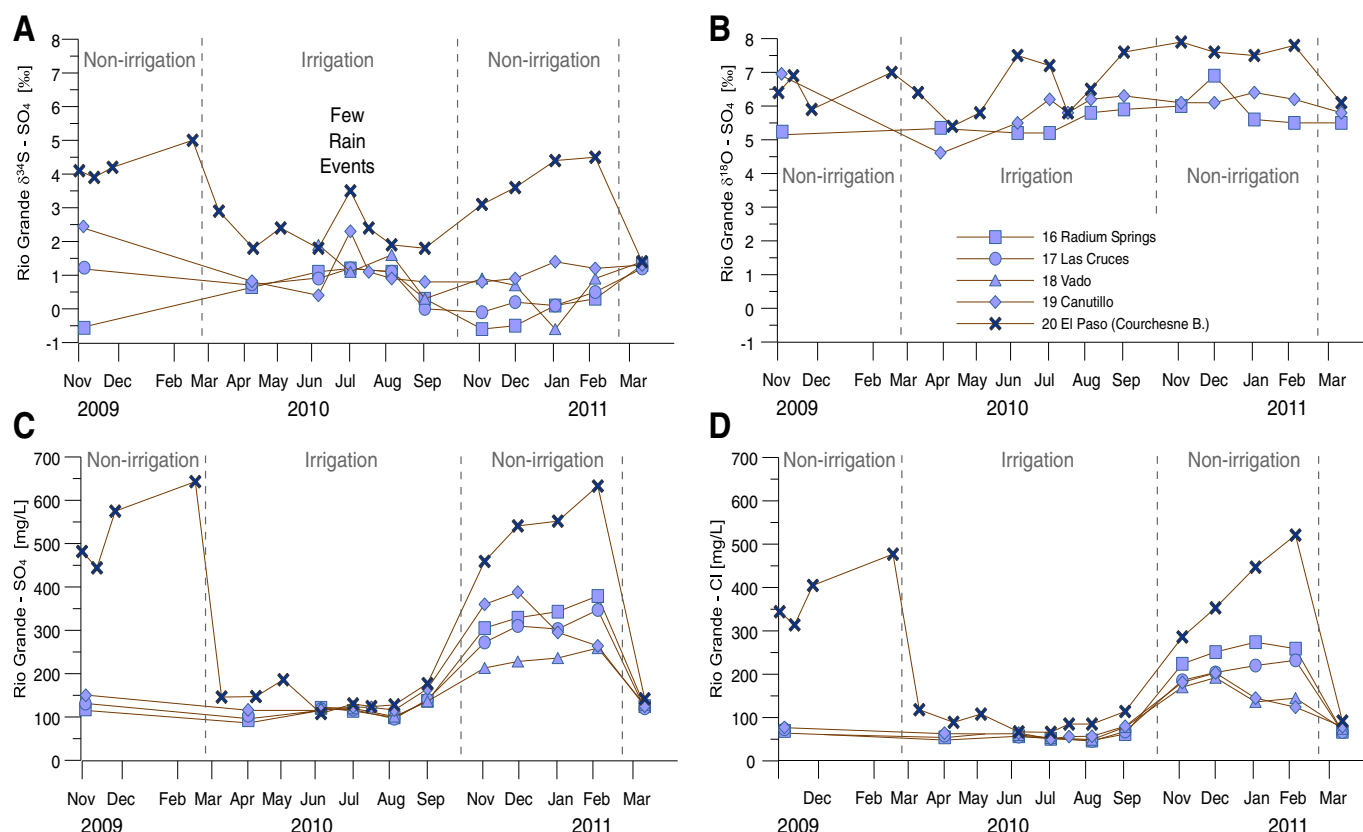


Fig. 5. Seasonal variations of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of SO_4 (A and B) in the Rio Grande of the Mesilla Valley between Nov 2009 and Mar 2011. For comparison, variations of SO_4 and Cl concentrations are presented (C and D). See Fig. 2 for the locations of sampling points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

except for the deepest packet of saline water (200 m) which showed very high Cl concentrations (9373 mg/L) but substantially lower SO_4 concentrations (1315 mg/L). Lack of direct mixing of the Rio Grande with saline end members was also observed for the relationship of SO_4 versus HCO_3^- (Fig. 3). Our observations are consistent with recent mass balance calculations done for the Middle Rio Grande (e.g., the Socorro basin) suggesting a minor (~5%) salinity increases due to leaking of localized brine pools originated from surface evaporation of endogenic fluids (Williams et al., 2013).

Geochemical data suggest that the surface water system, including the Rio Grande, drains, and wastewater inflows are all interrelated (Fig. 3). This is probably a result of mixing in the surface environment since the drain and city wastewaters are interconnected and flow directly into the Rio Grande. Moreover, the drains and city wastewater effluents showed higher salinity (average 2.48 mS/cm and 1.89 mS/cm, respectively) compared to the Rio Grande (average 1.36 mS/cm) (Suppl. Table 1), suggesting they are most likely important in increasing the salinity of the river.

5.1.2. Evidence from S and O isotope composition of SO_4

The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved SO_4 help in characterizing the sources of SO_4 and overall salinity in the Rio Grande. Dissolution/oxidation of bedrock sulfur (e.g., evaporites, sulfides) involves relatively small S and O isotope fractionations (<1–2‰; e.g., Krouse and Grinenko, 1991; Clark and Fritz, 1997; Krouse and Mayer, 2000). Therefore, the $\delta^{34}\text{S}$ of aqueous SO_4 , and in some cases $\delta^{18}\text{O}$ (e.g., dissolution of evaporites), are good environmental tracers to study mixing processes in hydrological systems (e.g., Knöller et al., 2005; Yuan and Mayer, 2012). This is particularly true for watersheds such as the Rio Grande which exhibit wide variations of isotope composition in SO_4 end members (Szyrkiewicz et al., 2015). In upstream locations near the Rio Grande

headwaters, the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of the Rio Grande SO_4 show relatively low values (ranges of -3.7 to $+0.7$ ‰ and -2.2 to $+4.5$ ‰, respectively) because of prevailing oxidation of the bedrock sulfides which are common in the Tertiary volcanic and Cretaceous sedimentary formations (Szyrkiewicz et al., 2015). However, in downstream locations, such as our study area, the bedrock is dominated by Paleozoic/Mesozoic sedimentary formations (usually of marine origin) with distinctively high $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values (ranges of $+8$ to $+12$ ‰ and $+10$ to $+12$ ‰, respectively; Lueth et al., 2005; Moore et al., 2008; Szyrkiewicz et al., 2011). Generally, the studied saline end members and groundwater of the semi-arid Rio Grande appear reflective of dissolution of local sedimentary rocks, with high $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ ($+7.9$ to $+10.5$ ‰ and $+6.8$ to $+11.2$ ‰, respectively; Fig. 7 and Szyrkiewicz et al., 2015). The geothermal water at Truth or Consequences (Loc. 77) had an anomalously low $\delta^{18}\text{O}$ of $+3.5$ ‰ compared to high $\delta^{34}\text{S}$ of $+9.1$ ‰ (Fig. 7), which probably resulted from high-temperature oxygen exchange between SO_4 and water (Szyrkiewicz et al., 2015).

The water from the Rio Grande and agricultural drains of the Mesilla and Hueco–Bolson basins showed considerably lower $\delta^{34}\text{S}$ (-0.6 to $+2.5$ ‰) and $\delta^{18}\text{O}$ ($+4.4$ to $+6.9$ ‰) than the possible groundwater endmembers (Figs. 7, 8). As with the major ion chemistry of the Rio Grande (described in Section 5.1.1; Fig. 3), the differences in $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ isotope distributions suggest minor inputs of sedimentary SO_4 from groundwater sources into the Rio Grande. Moreover, the seasonal variations of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ for the Rio Grande and the drains were relatively small in 2010 and 2011 (Figs. 5, 6). Generally, the isotopic signatures of the Rio Grande and its drains were similar to the upstream Elephant Butte and Caballo reservoirs ($\delta^{34}\text{S} +0.6$ to $+1.3$ ‰, $\delta^{18}\text{O} +3.2$ to $+5.5$ ‰) (Fig. 8), a major source of irrigation water for agriculture in the Las Cruces and El Paso areas (Locs. 16–19, 53–54).

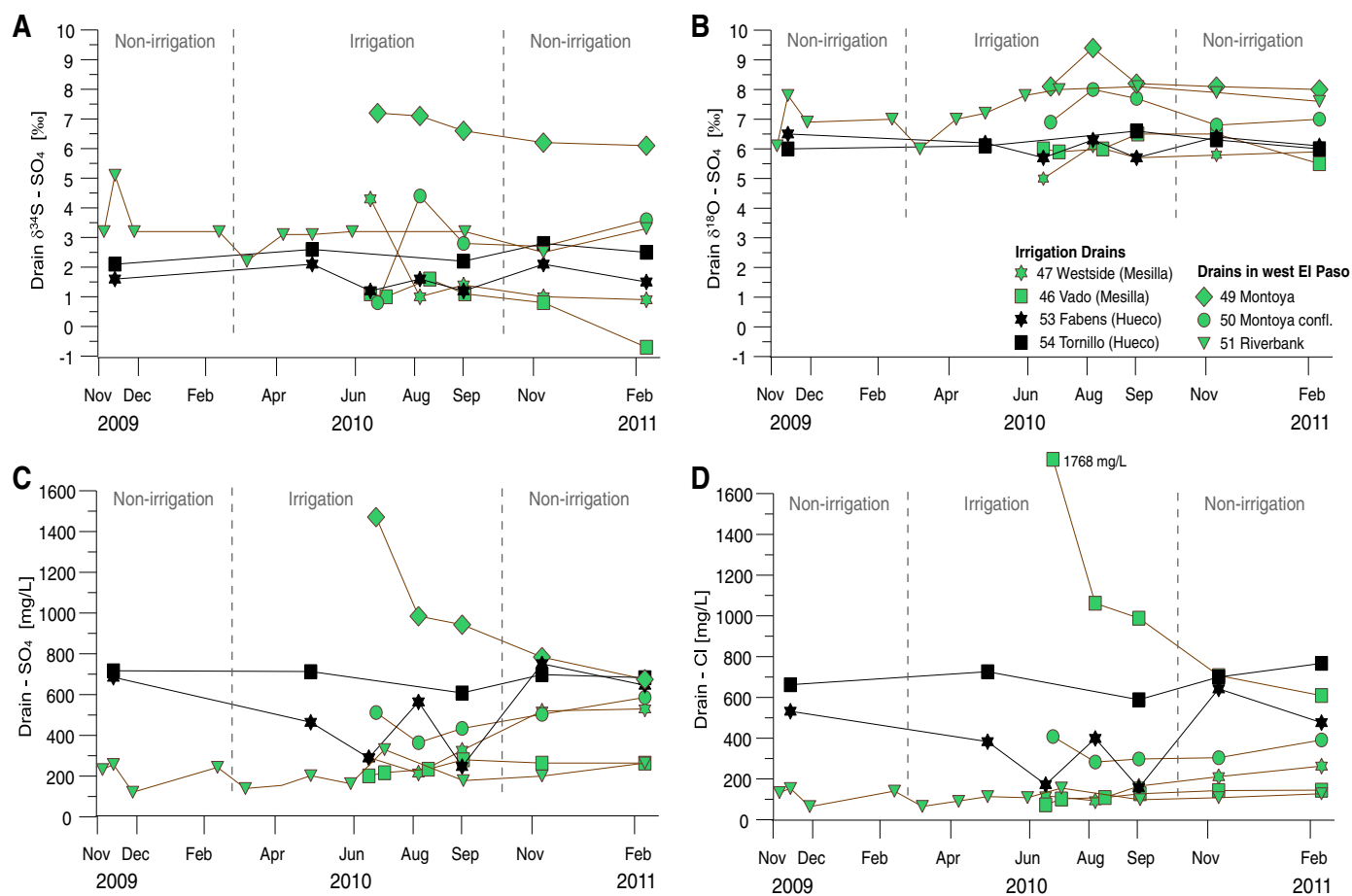


Fig. 6. Seasonal variations of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of SO_4 (A and B) of sampled drains between Nov 2009 and Feb 2011. For comparison, variations of SO_4 and Cl concentrations are presented (C and D). See Fig. 2 for the locations of sampling points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Nevertheless, some important localized contributions of sedimentary SO_4 were observed in the drains of west El Paso (Locs. 47–50) because their $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ were usually higher (+2.2 to +7.2‰ and

+6.0 to +9.4‰, respectively) compared to the Rio Grande and agricultural drains (Figs. 5A B, 6A B). We suggest that this might have resulted from both the watering of west El Paso (e.g., irrigation for urban

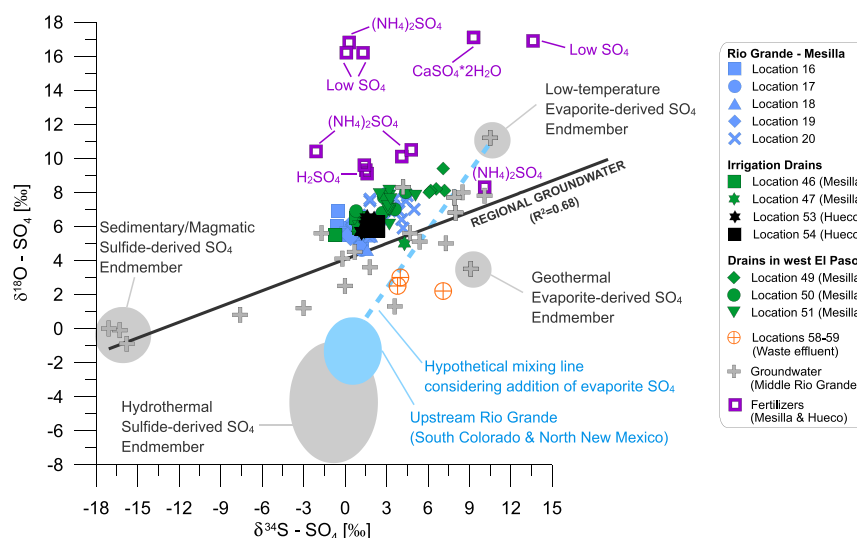


Fig. 7. Variation of $\delta^{34}\text{S}$ versus $\delta^{18}\text{O}$ in the Rio Grande, drains, fertilizers, saline groundwater, and waste effluents in the Mesilla and Hueco–Bolson basins. The gray regression line ($R^2 = 0.68$) between sulfide- and sulfate-derived SO_4 , and the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of regional groundwater, upstream Rio Grande, and sedimentary/hydrothermal sulfide-derived SO_4 endmembers are presented after Szyrkiewicz et al. (2015). The blue dotted line indicates hypothetical mixing line between the Rio Grande surface water and low-temperature evaporite-derived SO_4 which abundance increases downstream. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

landscapes and golf fields) with municipal aquifer water, carrying the SO_4 with higher $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ from dissolution of local sedimentary rocks enriched in Paleozoic/Mesozoic gypsum and anhydrite of marine origin, and further interaction of this water with the sedimentary bedrock.

Additionally, in west El Paso (Loc. 20) some agricultural drains intersect the groundwater table of natural salt flats (Fig. 2). Salt flats are low-elevation sites covered with various evaporative minerals (e.g., sulfates, chlorides, carbonates). They are attributed to an elevated saline groundwater (e.g., brine) that is continuously evaporating as it approaches the ground surface. This type of settings is common in the Rio Grande rift because of high surface temperatures and the closed-drainage structures of many of the topographic basins (e.g., Langford, 2003). The source of water in salt flats is surface and groundwater recharge from surrounding mountain ranges and upwelling groundwater at the basin terminus. The shallow groundwater of the salt flat in west El Paso is characterized by high $\delta^{34}\text{S}$ of +12.4‰ (Moore et al., 2008) which suggests major SO_4 sources from dissolution of local sedimentary rocks. The $\delta^{34}\text{S}$ alone cannot be used for distinguishing between deep and shallow groundwater flows in this area because similar sedimentary strata crop out at the surface and are buried in the basin center. Nevertheless, this salt flat is intersected by the Montoya drain (Loc. 50), which conveys water from the upstream irrigation district (Newmexas drain at Loc. 48) and the storm/residential drains of west El Paso (Loc. 49). Because of high groundwater salinity in the salt flat (e.g., $\text{SO}_4 \sim 5100\text{--}6200\text{ mg/L}$, $\text{Cl} \sim 7900\text{--}18,000\text{ mg/L}$; Moore et al., 2008), the Montoya Drain had the highest SO_4 and Cl concentrations (700 to 1600 mg/L and 600 to 1750 mg/L, respectively) and $\delta^{34}\text{S}$ (+6.1 to +7.0‰) among the studied drains (Fig. 6). Consequently, the concentrations of major ions usually increased in the Rio Grande below the confluence with Montoya drain (Location 20, Fig. 5C, D) and were followed by important increases of $\delta^{34}\text{S}$ (Fig. 5A), particularly during the non-irrigation

season (+2 to +5‰) when the stream flows were reduced and less water was available in the Rio Grande for dilution. Using the changes of $\delta^{34}\text{S}$ between Canutillo (Loc. 19) and west El Paso (Loc. 20), S isotope mass balance calculations suggest that in the dry fall/winter seasons the Montoya drain ($\delta^{34}\text{S} \sim +7\text{‰}$) may contribute up to ~60% of SO_4 (derived from the evaporative brine of the salt flat) to the Rio Grande in west El Paso. This contribution is reduced to only ~20% in the irrigation season when stream flows greatly increase due to water releases from the upstream reservoirs.

5.1.3. Comparison of SO_4 fluxes from evaporative brine versus irrigation runoff

In order to compare the SO_4 fluxes between the surface evaporative brine such as that observed in west El Paso (Loc. 20) and the typical irrigation runoff, we also calculated seasonal SO_4 fluxes of the Tornillo drain south of El Paso (Loc. 54 in Fig. 2) between 2009 and 2011. The Tornillo drain had the highest SO_4 concentrations (608 to 717 mg/L) among the studied agricultural drains (Fig. 6C). The Tornillo drain, however, does not show any surface evidence of natural salt flats in the nearby area. The relatively low $\delta^{34}\text{S}$ of the Tornillo drain and its small seasonal variation (+2.2 to +2.8‰) also suggests that evaporite-derived SO_4 was negligible (Fig. 6A). Generally, the SO_4 fluxes of the Tornillo drain varied over the narrow range of 62 to 89 metric tons/day between 2009 and 2011 (Fig. 9). In contrast, the Rio Grande in west El Paso at Location 20 showed much wider seasonal variations of SO_4 fluxes (Fig. 9). Considerably higher SO_4 fluxes were observed during irrigation (~200 to 450 metric tons/day) compared to smaller fluxes in the fall/winter (~30 to 80 metric tons/day) when the stream flows were reduced but the inflow from the evaporative brine (salt flat) via the Montoya drain was the highest. Using the estimated SO_4 contributions from S isotope mass balance (20 to 60%; see Section 5.1.2), we calculated that the SO_4 flux from the Montoya drain

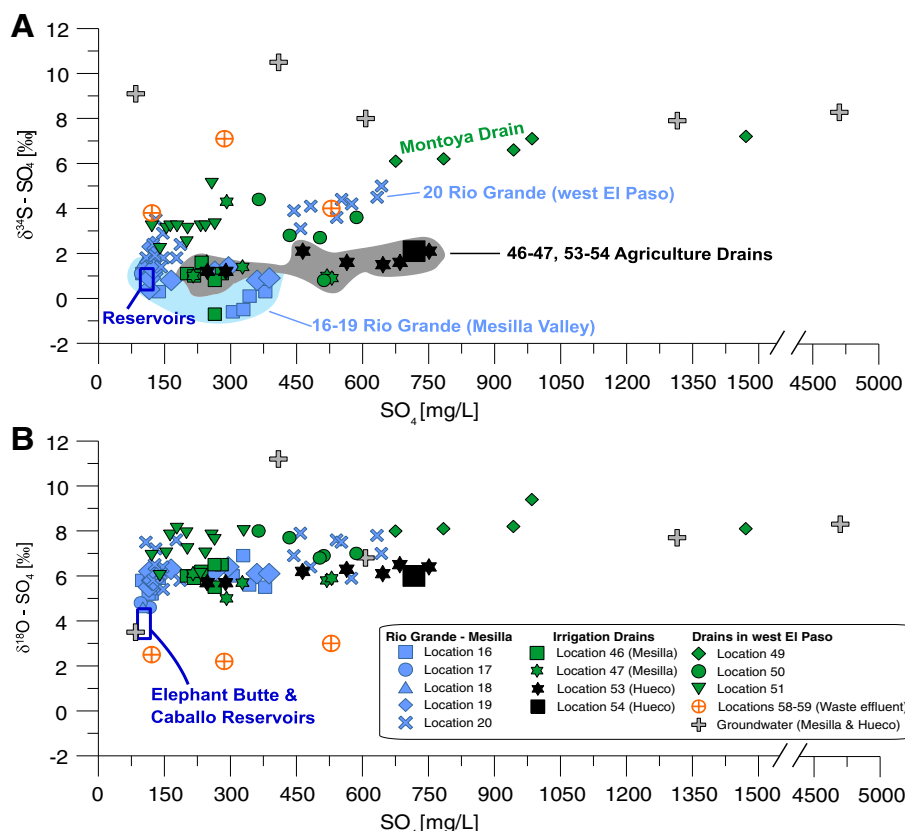


Fig. 8. Variations of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ versus SO_4 concentrations in the Rio Grande, agricultural/city drains, groundwater, waste effluents, and two major reservoirs in central/south New Mexico. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

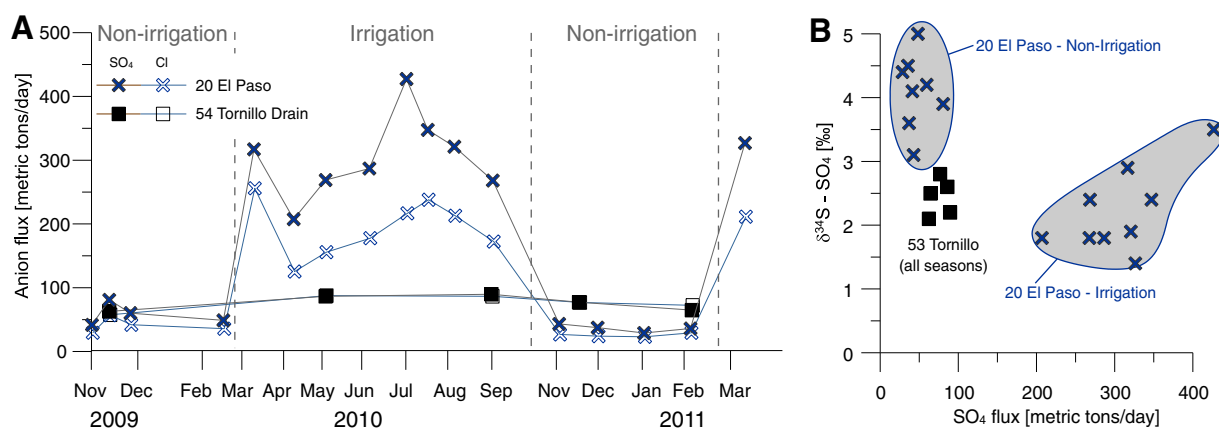


Fig. 9. (A) Fluxes of SO_4 and Cl in the Rio Grande at west El Paso (Loc. 20) and in the Tornillo Drain (Loc. 54) between Nov 2009 and Feb 2011. (B) Comparison of SO_4 fluxes versus $\delta^{34}\text{S} - \text{SO}_4$ symbols and locations are same as on (A). See Fig. 2 for the locations of sampling points.

accounted for at least ~18–48 metric tons/day of SO_4 during the non-irrigation and ~40–90 metric tons/day during the irrigation season. Therefore, the amount of SO_4 loading to the Rio Grande via the Montoya drain is ~35% less than the SO_4 flux attributable to the Tornillo drain. However, the size of the salt flat intersected by Montoya drain is considerably smaller (~2 km²) compared to the Tornillo drainage area (~190 km²). Therefore, we infer that (at least in one case identified here) poorly-designed agricultural drains intersecting the water table of localized evaporative brines are important contributors of salts to the Rio Grande.

5.1.4. Evidence from U isotopes

In order to better distinguish between shallow and deeper groundwater sources (upwelling) in the studied stretch of the Rio Grande, we also measured the ($^{234}\text{U}/^{238}\text{U}$) activity ratios for the water samples collected in November 2009 and April 2010. Generally, groundwater that has experienced a deeper circulation history can be distinguished from surface water by higher ($^{234}\text{U}/^{238}\text{U}$) ratios (Kronfeld, 1974; Kronfeld et al., 1994; Chabaux et al., 2003). This is due to precipitation of small amounts of U from water when groundwater moves through a redox front in the aquifer (Langmuir, 1978; Drever, 1997) and enhanced transfer of alpha-recoil ^{234}U from the U-rich aquifer rock surfaces back to the U-depleted groundwater (Kronfeld, 1974; Kronfeld et al., 1994). Accordingly, in our study the deeper saline end members from Truth or Consequences had a higher ($^{234}\text{U}/^{238}\text{U}$) ratio of 2.65, as did the saline groundwater from Fabens ($^{234}\text{U}/^{238}\text{U}$ of 2.54) (Fig. 10). In contrast, the $^{234}\text{U}/^{238}\text{U}$ ratios were considerably lower in the Montoya drain intersecting the evaporative brine of the salt flat (~1.55), the Rio Grande (~1.62 to 1.88), the Tornillo agricultural drain (~1.35), and fertilizers (~1.00) (Fig. 10). This suggests that the most important salt sources influencing the Rio Grande in the study area are from shallow water circulation as opposed to deep inflows of saline fluids. The small increases of the $^{234}\text{U}/^{238}\text{U}$ ratios, up to 2.13 and 2.06, were only observed in the Rio Grande at Truth or Consequences (Loc. 77) and at Canutillo (Loc. 19), respectively, during the non-irrigation season of 2009 (Fig. 10). Because the $\delta^{34}\text{S}$ also importantly increased (+4.2‰) in Truth or Consequences, we attribute the increasing ($^{234}\text{U}/^{238}\text{U}$) ratios to the direct inflow of geothermal water ($\delta^{34}\text{S} + 9.1\text{‰}$) to the Rio Grande from the spa resorts which are common in this area. However, at Canutillo the $\delta^{34}\text{S}$ was considerably lower (+2.7‰) compared to the regional groundwater (>+8‰; Szyrkiewicz et al., 2011). In this area, aquifer groundwater is often used to support irrigation with the Rio Grande surface water. Therefore, the subsequent lowering of $\delta^{34}\text{S}$ of the aquifer groundwater is caused by mixing with low $\delta^{34}\text{S}$ of the Rio Grande water. Given that the Rio Grande at Canutillo (Loc. 19) completely dries out during the non-irrigation season, we suggest that the increasing $^{234}\text{U}/^{238}\text{U}$ activity ratios in this

location are mainly controlled by shallow irrigation return flows which represent a portion of the aquifer groundwater pumped for agricultural activity. Considerable inflow of deep groundwater would be accompanied by higher increases of $\delta^{34}\text{S}$, but this scenario does not fit the data.

5.2. Additional indication of the importance of surface processes

5.2.1. Agricultural impact on SO_4 cycling and microbial processes

Although the SO_4 concentrations considerably increased in the study area with the downstream flow in the Rio Grande and agricultural drains (Fig. 8), they were not accompanied by important increases of $\delta^{34}\text{S}$ which varied over a narrow range of +0.6 to +2.5‰ (Figs. 5A, 8A). The one exception was in west El Paso (Loc. 20) for which the increasing $\delta^{34}\text{S}$ of the Rio Grande (Fig. 5A) resulted from surface inflow of evaporative brine via the Montoya drain which intersects groundwater table of natural salt flat (see Section 5.1.2). In contrast, the $\delta^{18}\text{O}$ of SO_4 showed larger increases versus SO_4 concentrations and relative to the distance from the Rio Grande headwaters (from -2.2 to +7.1‰) and from the Elephant Butte and Caballo reservoirs (from +3.2 to +7.1‰) (Figs. 7, 8B). Moreover, on the plot of $\delta^{34}\text{S}$ versus $\delta^{18}\text{O}$ the studied water samples were usually concentrated toward higher $\delta^{18}\text{O}$ values and above both 1) the regression line defining mixing trend of sulfide- and evaporite-derived SO_4 and 2) the hypothetical mixing line considering addition of low-temperature evaporite-derived SO_4 to the Rio Grande surface water (Fig. 7). We suggest that this is indicative of additional SO_4 inputs with distinctive high $\delta^{18}\text{O}$ values into the studied water samples. Previous investigators have shown the importance of SO_4 contributions from the application of fertilizers in the areas affected by agriculture (Mizota and Sasaki, 1996; Mallén, 2000; Moncaster et al., 2000; Victòria et al., 2004; Brenot et al., 2007). In the Rio Grande watershed, the S-rich fertilizers such as ammonium sulfate, elemental sulfur, and sulfuric acid are commonly applied to agricultural fields to manage salinity hazards. Except for one sample of ammonium sulfate with higher $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ (+10.1 and +8.3‰), these fertilizers showed relatively low $\delta^{34}\text{S}$ of -2.1 to +4.8‰ and high $\delta^{18}\text{O}$ of +9.1 to +16.8‰ (Fig. 7; Table 1). Therefore, the addition of fertilizers in this stretch of the Rio Grande might account for the increase in $\delta^{18}\text{O}$ with very little influence on the $\delta^{34}\text{S}$ as a function of increasing SO_4 concentrations (Fig. 8). Other less-soluble fertilizers such as soil amendment gypsum had higher $\delta^{34}\text{S}$ of +5.1 to +13.6‰ in addition to high $\delta^{18}\text{O}$ (Table 1), thus, they could not be distinguished from dissolution of bedrock evaporites with gypsum and anhydrite with similarly high $\delta^{34}\text{S}$ of +8 to +12‰ (Lueth et al., 2005; Moore et al., 2008; Szyrkiewicz et al., 2011).

The $\delta^{18}\text{O}$ of SO_4 of the Rio Grande and drains in the study area was usually higher (+4.4 to +6.9‰) than the $\delta^{18}\text{O}$ of the Rio Grande in the Elephant Butte and Caballo reservoirs (+3.2 to +4.0‰) but it

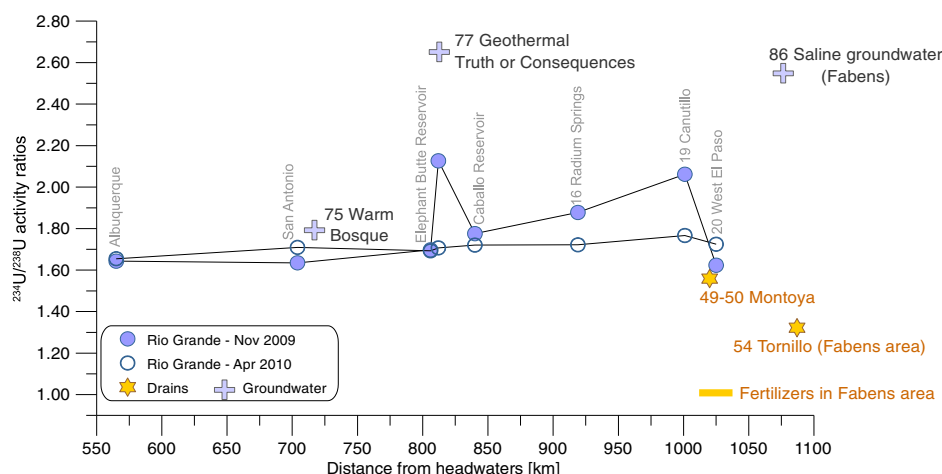


Fig. 10. Seasonal variations of ($^{234}\text{U}/^{238}\text{U}$) activity ratios in the Rio Grande for Nov 2009 (non-irrigation) and Apr 2010 (irrigation) compared to the selected water samples of groundwater with elevated salinity, drains, and U-rich fertilizers. Numbers above symbols indicate sampling locations shown in Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

was lower compared to fertilizers (+8.3 to +16.8‰) and low-temperature aquifer water (+6.8 to +11.2‰) (Figs. 7, 8). This implies that in addition to mixing between different SO_4 end members (e.g., evaporites, fertilizers) another mechanism may be causing a lowering of $\delta^{18}\text{O}$ in the studied area. Since up to 70–90% of the Rio Grande water undergoes infiltration through agricultural soils during irrigation (Ellis et al., 1993), some lowering of $\delta^{18}\text{O}$ might be more controlled by microbial processes in soils (e.g., Mayer et al., 1995; Shanley et al., 2005; Yuan and Mayer, 2012). Assimilatory microbial SO_4 reduction and re-oxidation in soils usually lead to lowering of initial $\delta^{18}\text{O}$ in SO_4 because some oxygen atoms in the SO_4 are replaced by oxygen from soil water with negative $\delta^{18}\text{O}$. These processes typically have only a small effect on the $\delta^{34}\text{S}$ values of SO_4 unless dissimilatory bacterial sulfate reduction occurs (Mitchell et al., 1998). The latter causes substantial increases of $\delta^{34}\text{S}$ followed by a decrease of SO_4 concentration in aqueous environment (e.g., Canfield, 2001). Because the $\delta^{34}\text{S}$ of the Rio Grande did not change much despite increasing SO_4 concentrations (100 to 750 mg/L) (Fig. 8), it is clear that dissimilatory microbial SO_4 reduction had a negligible impact on the isotope composition of the Rio Grande SO_4 . Generally, the observed lowering of $\delta^{18}\text{O}$ in Rio Grande and drains is in a good agreement with similar pattern observed by Yuan and Mayer (2012) in the adjacent watershed of the Pecos River in eastern New Mexico. They reported that up to 63% of dissolved SO_4 in the Pecos River has been recycled in the irrigated soils causing the $\delta^{18}\text{O}$ decreases by 5‰.

An alternate or perhaps additional mechanism of lowering of $\delta^{18}\text{O}$ could be inflows of SO_4 from waste effluents with low $\delta^{18}\text{O}$ of +2.2 to 3.0‰ in Las Cruces and El Paso (Figs. 7, 8). However, the effluent SO_4 had considerably higher $\delta^{34}\text{S}$ of +3.8 to +7.1‰ compared to the Rio Grande and agricultural drains (−0.6 to +2.5‰), thus, this source is inconsistent with the consistency of the $\delta^{34}\text{S}$ in the Rio Grande and drains (Figs. 6, 8). Moreover, the concentrations of SO_4 were importantly higher in the studied drains (~250 to 1500 mg/L) compared to waste effluents (~120 to 530 mg/L) that we attribute to increased evaporation during flood irrigation. This, in turn, indicates that the inflows of drain SO_4 are more important in the Rio Grande compared to municipal sources as inferred using S and O isotope data alone.

5.2.2. Anthropogenic NO_3 contributions

Prevailing shallow recharge to the Rio Grande is also inferred from the elevated NO_3 concentrations along the Mesilla basin, from <1 to 46 mg/L (Fig. 4A). The measurements of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in NO_3 on the Rio Grande water samples in Truth or Consequences (Loc. 77) and west El Paso (Loc. 20) were consistent with the variation of $\delta^{15}\text{N}$ and

$\delta^{18}\text{O}$ reported for manure and septic tanks undergoing denitrification (Fig. 4C; e.g., Kendall, 1998). The highest NO_3 concentrations (27 to 46 mg/L) were observed during fall 2010 in Vado (Loc. 18), located ~25 km downstream from the waste water treatment plant in Las Cruces (Loc. 57) (Fig. 4A). This plant showed considerably higher NO_3 (90 to 110 mg/L) compared to other plants in west El Paso (22–46 mg/L; Suppl. Table 1). In Vado, however, the NO_3 concentrations substantially decreased to <1 mg/L closer to the end of non-irrigation season (Fig. 4A). Most likely, this was due to changing hydrological conditions. In January and February of 2011 there was no continuous surface water flow in the Rio Grande between Las Cruces and Vado. Instead, only localized ponded water was present in the Rio Grande channel. Consequently, our results (Fig. 4A) suggest that particularly during the winter there is important infiltration of the Las Cruces waste effluent into the Rio Grande alluvial aquifer system.

Alternatively, in Vado the elevated NO_3 contributions might be sourced by runoff from several dairy farms located ~2–3 km east from the Rio Grande. Nevertheless, our sampling point in Vado (Loc. 18) was located upstream from the dairy farms. Therefore, the observed increases of NO_3 in the Rio Grande during fall 2010 at Vado (Fig. 4A) had to be mainly controlled by municipal waste water from Las Cruces since this was the largest measured contributor of NO_3 in the nearby area. In Vado, the waste water NO_3 contributions to the Rio Grande became proportionally higher in the fall because of the decreased flows related to the reduced releases of surface water from upstream reservoirs.

Generally, the NO_3 and PO_4 concentrations of the studied drains were considerably lower (<1 to 3 mg/L and 0.06 to 0.45 mg/L, respectively) compared to the waste effluents (22 to 110 mg/L and 1 to 16 mg/L, respectively) (Fig. 4B), suggesting smaller NO_3 and PO_4 contributions from agricultural sources to the Rio Grande in the Mesilla basin. It is noteworthy that the agricultural drains south of El Paso in the Hueco–Bolson basin (Locs. 53–54, Fig. 2) had considerably higher NO_3 and PO_4 concentrations (4 to 13 mg/L and 0.2 to 2 mg/L, respectively) compared to the Mesilla's drains. While application of different fertilizers enriched in nitrogen and phosphorous might be locally important, the increasing effluent inflows into the irrigation canals from three waste treatment plants in El Paso might also be influencing higher NO_3 and PO_4 loadings in the studied drains at Locations 53 and 54. Because of prevailing dry conditions, particularly in this area, the waste effluents represent a large fraction of the stream flow in the irrigation canals. Therefore, urban sources (e.g., waste effluents) are likely important in increasing NO_3 and PO_4 loadings in the irrigation water used in downstream locations south of El Paso. The latter is supported by the measured $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3 in the drains at Locations 53 and 54

which were within the range observed for the Rio Grande and the septic waste end member (Fig. 4C). Since the waste effluent from Juarez, Mexico discharges to the Rio Grande ~160 km south of El Paso, we did not consider it as important in increasing NO_3 and PO_4 loads in the studied drains at Locations 53 and 54 situated closer to El Paso (~50 km). Additionally, the U.S. and Mexican irrigation canals and drains are not connected with each other, thus, they can be treated separately in this interpretation.

5.3. Evaporation and evolution of water chemistry

Irrigation water applied to agricultural fields is consumed by crops (transpires or becomes plant biomass), infiltrates to groundwater aquifer, and evaporates from the surface and/or the near-surface soil. The evaporative loss is particularly important in arid zones because of high annual surface temperatures and low air humidity (e.g., Sheta et al., 2000; Van den Akker et al., 2011; Jafari et al., 2012). Additionally, ponding of water and evaporation in topographic depressions is important in increasing surface salt accumulation (Acosta et al., 2011; van den Akker et al., 2011).

In the Rio Grande study area, the water losses due to evapotranspiration may reach up to 70% (Phillips et al., 2003). Majority of the irrigated lands in the studied area have fine-textured, smectitic, clay soils that have low permeability (e.g., Ganjgunte et al., 2011). This means that infiltration rates are slow and there is more time for the irrigation water to evaporate. Therefore, evapotranspiration is likely a primary driver in increasing the concentrations of salts in this region of the Rio Grande. Since evapotranspiration does not considerably fractionate S isotopes, the SO_4 and Cl concentrations of the Rio Grande were able to greatly increase (Fig. 5C, D), while at the same time the changes in $\delta^{34}\text{S}$ were small (Fig. 5A).

Salt mobility related to changes of seasonal conditions (e.g., irrigation, rainfall, evaporation) have been recognized as important for salt loads and storage in arid zones (Yuan and Miyamoto, 2005, 2008; Yuan et al., 2007; Acosta et al., 2011). For example, secondary salts such as carbonates (CaCO_3), sulfates (gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, thenardite Na_2SO_4) and chlorides (halite NaCl) are commonly found in arid soils (e.g., Sheta et al., 2000; Graham and O'Geen, 2010; Jafari et al., 2012). The formation of these salts is mainly controlled by mineral solubility (Sheta et al., 2000; Jafari et al., 2012) and environmental conditions via changes of the evaporation and dilution rates (Mees, 2003). Less soluble calcite precipitates first compared to the more soluble gypsum (followed by other phases like thenardite and halite which precipitate later from more concentrated solutions in evaporative brine pools).

In our study area, the formation of secondary calcite commonly occurs in the shallow subsurface of agricultural soils (6–10 wt.%; Cox, 2012) and substantially decreases the soil permeability of the irrigated land. For this reason sulfuric acid with low $\delta^{34}\text{S}$ and high $\delta^{18}\text{O}$ (Table 1) is sometimes used by farmers to lower the pH of irrigation water and dissolve secondary calcite. Consequently, all of the analyzed Rio Grande and drain water samples were usually saturated (or super-saturated) with respect to calcite (SI: 0 to +1) (Fig. 11). However, the water samples were undersaturated with respect to gypsum (SI: -1 to 0), and greatly undersaturated with respect to halite (SI: -8 to -6) and thenardite (SI: -10 to -8). We suggest that the evolution of water chemistry toward $\text{Na-SO}_4\text{-Cl}$ in the Rio Grande watershed is attributable to the fact that calcite is precipitating in the system. This is supported by higher concentrations of SO_4 , Cl, and Na (~500–750 mg/L, 300–900 mg/L, and 100–600 mg/L, respectively) compared to lower (and relatively consistent) concentrations of Ca and HCO_3 (~60–200 mg/L and 200–250 mg/L, respectively) in the studied Rio Grande and drain water samples (see the deviation from the evaporation trend in Fig. 3B). Most likely, the observed salinization effect is intensified by flood irrigation which exposes more water to evaporative concentration and subsequent salt accumulation (e.g., calcite) in the shallow soil zone of irrigated land.

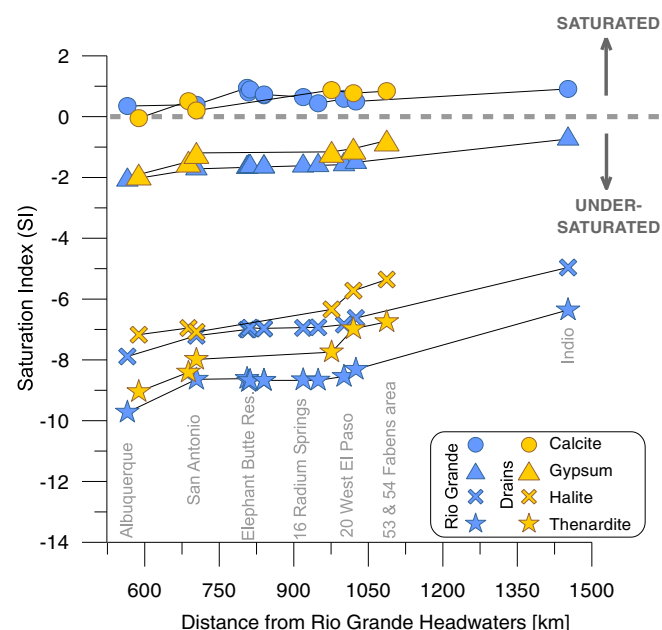


Fig. 11. Calculated average saturation indices for calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), thenardite (Na_2SO_4) and halite (NaCl) with respect to distance downstream using PHREEQ™ (Parkhurst and Appelo, 1999). Averages were calculated from samples collected at the same locations during different periods between 2009 and 2011 (Suppl. Table 1; Szyrkiewicz et al. 2015). For clarity, error bars were not included. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

6. Summary

6.1. Major conclusions

The chemical and isotope data for the semi-arid reach of the Rio Grande watershed investigated in our study indicate that surface processes lead to the main increases of SO_4 and overall salinity in the studied area of the Rio Grande. Natural inflows of saline groundwater to the Rio Grande and drains appeared to be negligible in the investigated seasons. The important inflows of highly saline water to the Rio Grande via the Montoya drain are attributable to localized surface brines forming naturally in low-elevation areas (e.g., salt flats) due to evaporation. This was recorded by considerable increases of both $\delta^{34}\text{S}$ of SO_4 , concentration of major ions, and lowering of the ($^{234}\text{U}/^{238}\text{U}$) activity ratios in the Rio Grande. The application of sulfur-rich fertilizers with low $\delta^{34}\text{S}$ and high $\delta^{18}\text{O}$ might be also responsible in part for additional increases of SO_4 loads into the irrigation return flows and, thus, the Rio Grande. We additionally infer that during irrigation, SO_4 undergoes substantial microbial recycling in the soil environment leading to decreases in $\delta^{18}\text{O}$.

The hydrochemical evolution of the Rio Grande waters toward $\text{Na-SO}_4\text{-Cl}$ -rich composition is primarily caused by high evapotranspiration rates and increases in temperature leading to the precipitation of calcite. The Ca and HCO_3 are firstly consumed by calcite precipitation because of its lower solubility compared to other salts like gypsum, thenardite and halite, thus, leaving behind water enriched in Na, SO_4 and Cl. Agricultural practices during flood irrigation additionally intensify concentrative evaporation and, in turn, increase water salinity of the Rio Grande watershed.

6.2. Synthesis and recommendations

Increasing urban water demand coupled with expected climate changes will most likely result in the increased variability of water supply, water scarcity, and therefore the challenges of water sustainability within the context of increasing salinity in arid rivers such as the Rio Grande (Ragab and Prudhomme, 2002; Borrok and Engle, 2014). For

example, leaching of salts from agricultural soils will become increasingly important to avoid substantial salt-related crop yield losses (Jia et al., 2011; Connor et al., 2012; Rasouli et al., 2012).

In the studied portion of the semi-arid Rio Grande there is no evidence to suggest that the upwelling of saline groundwater near the river has any impact on salt loads, thus, developing management strategies to address this salt input is impractical. Conversely, most of the salt loads appear to be attributable to near-surface processes. Therefore, reducing evaporation of irrigation water would improve efficiency of water use, leaching of salts to deeper depth within soil profile, and decrease salinization. Most likely, this could be best achieved by improved scheduling of irrigation and adoption of sub-surface drip irrigation in turfed areas (e.g., Sevostianova et al., 2011; Ganjegunte et al., 2012; Ganjegunte et al., 2013; Payero et al., 2005). Developing alternative water sources such as desalinated brackish groundwater and reclaimed municipal wastewater could conserve and extend the available freshwater resources. Mostly, the sequential and/or alternative irrigation with freshwater in the fields currently irrigated with brackish groundwater and/or marginal water (e.g., saline water, wastewater, and runoff water) could help in preventing salt buildup in shallow soil environments.

In recent years, desalination of the Rio Grande surface water has been considered by some state agencies to reduce salt loads on agricultural fields in south New Mexico and west Texas (e.g., U.S. Army Corps of Engineers, 2011). However, desalination systems are still expensive. Furthermore, the process itself generates saline waste water that would have to be disposed in the surface environment already affected by higher salt loads, unless injection of waste water to deep surface is possible. Our study shows that some of the studied drains intersect the water table of natural settings with surface brines (e.g., salt flats). Therefore, a potentially more economical approach would be re-designing the old drainage system, particularly in west El Paso, to prevent unnecessary surface inflow of highly saline water into the Rio Grande. Similar solution could be implemented in the areas where highly saline geothermal water flows directly to the Rio Grande from the spa (bath) houses (e.g., Truth or Consequences, New Mexico).

Acknowledgments

This study was supported by a State of Texas Norman Hackerman grant 003661-0046-2009 and NSF grant 0838120 (D. Borrok), and partially by grants from UTEP URI 14-6485-4651 (A. Szyrkiewicz) and NSF EAR 1348971 (A. Szyrkiewicz, L. Ma). G. Skrzypek was supported by a Future Fellowship from the Australian Research Council (FT110100352). We greatly thank the UTEP students Dennise Drury, Wendy De Leon, Nicole Kyger, Susan Aranda, Ana Lu Gutierrez, and Ian Cappel for the field/lab assistance and Ben Underwood from Indiana University for assistance with sulfur isotope analysis. Phil Goodell provided assistance with chemical analysis of fertilizers by the Actlabs Life Sciences in Ancaster, Ontario, Canada. The discussions with Scott Anderholm, Malynda Cappel, Talon Newton, Dave Love, Joel Gilbert, John Hawley, Rip Langford, Zhuping Sheng, John Sorrell, Cody Walker and the participation of first author in the Rio Grande Coalition meetings significantly helped in the planning of sampling strategy and understanding salinity challenges in the Rio Grande region. The field assistance of the El Paso Desalination Plant is also greatly appreciated. Review comments of B. Brunner and two anonymous reviewers greatly improved the clarity of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2015.05.023>.

References

- Acosta, J.A., Faz, A., Jansen, B., Kalbitz, K., Martínez-Martínez, S., 2011. Assessment of salinity status in intensively cultivated soils under semiarid climate, Murcia, SE Spain. *J. Arid Environ.* 75, 1056–1066.
- Anderholm, S.K., 2002. Water-quality assessment of the Rio Grande Valley, Colorado, New Mexico and Texas – surface water quality, shallow groundwater quality, and factors affecting water quality in the Rincon Valley, south-central New Mexico, 1994–95. U.S.G.S. Water-Resources Investigations Report 02-4188, p. 125.
- Borrok, D.M., Engle, M.A., 2014. The role of climate in increasing salt loads in dryland rivers. *J. Arid Environ.* 111, 7–13.
- Brenot, A., Carignan, J., France-Lanord, C., Benoit, M., 2007. Geological and land use control on $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of river dissolved sulfate: the Moselle river basin, France. *Chem. Geol.* 244, 25–41.
- Canfield, D.E., 2001. Biogeochemistry of sulfur isotopes. In: Valley, J.W., Cole, D.R. (Eds.), *Stable Isotope Geochemistry*. Mineralogical Society of America 43. Blacksburg, VA, pp. 607–636.
- Casciotti, K.L., Sigman, D.M., Galanter Hastings, M., Bohlke, J.K., Hilkert, A., 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Anal. Chem.* 74, 4905–4912.
- Chabaux, F., Riotte, J., Dequincey, O., 2003. U–Th–Ra fractionation during weathering and river transport. *Rev. Mineral. Geochem.* 52, 533–576.
- Clark, K.I., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, New York, p. 328.
- Connor, J.D., Schwabe, K., King, D., Knapp, K., 2012. Irrigated agriculture and climate change: the influence of water supply variability and salinity on adaptation. *Ecol. Econ.* 77, 149–157.
- Cox, C.L., 2012. Evaluation of Soil Sustainability Along the Rio Grande in West Texas: Changes in Salt Loading and Organic Nutrients Due to Farming Practices (M.S. Thesis). University of Texas at El Paso.
- Drever, J.I., 1997. *The Geochemistry of Natural Waters: Surface and Groundwater Environments* (ISBN-10: 0132727900).
- Ellis, S.R., Levings, G.W., Carter, L.F., Richey, S.F., Radel, M.J., 1993. Rio Grande Valley, Colorado, New Mexico, and Texas. *J. Am. Water Res. Assoc.* 29, 617–648.
- Ganjegunte, G.K., Sheng, Z., Braun, R.J., 2011. Salinity management using an anionic polymer in a pecan field with calcareous-sodic soil. *J. Environ. Qual.* 40, 1314–1321.
- Ganjegunte, G.K., Sheng, Z., Clark, J.A., 2012. Evaluating accuracy of soil water sensors for irrigation scheduling to conserve freshwater. *Appl. Water Sci.* 2, 119–125.
- Ganjegunte, G.K., Leinauer, B., Schiavon, M., Serena, M., 2013. Using electromagnetic induction to determine soil salinity and sodicity in turf root zones. *Agron. J.* 105, 836–844.
- Graham, R.C., O'Geen, A.T., 2010. Soil mineralogy trends in California landscape. *Geoderma* 154, 418–437.
- Gutzler, D.S., Robbins, T.O., 2010. Climate variability and projected change in the western United States: regional downscaling and drought statistics. *Clim. Dyn.* <http://dx.doi.org/10.1007/s00382-010-0383-7>.
- Hibbs, B.J., Merino, M., 2006. Geologic sources of salinity in the Rio Grande aquifer near El Paso, Texas. *New Mexico J. Sci.* 44, 1–17.
- Hogan, F.M., Phillips, F.M., Mills, S.K., Hendrickx, J.M.H., Ruiz, J., Chesley, J.T., Asmerom, Y., 2007. Geologic origins of salinization in semi-arid river: the role of sedimentary basin brines. *Geology* 35, 1063–1066.
- Jafari, H., Raesi, E., Hoehn, E., Zare, M., 2012. Hydrochemical characteristics of irrigation return flow in semi-arid regions of Iran. *Hydrol. Sci. J.* 57, 173–185.
- Jia, Z., Luo, W., Xie, J., Pan, Y., Chen, Y., Tang, S., Liu, W., 2011. Salinity dynamics of wetland ditches receiving drainage from irrigated agricultural land in arid and semi-arid regions. *Agric. Water Manag.* 100, 9–17.
- Keller, G.R., Baldrige, W.S., 1999. The Rio Grande rift: a geological and geophysical overview. *Rocky Mt. Geol.* 34, 121–130.
- Keller, G.R., Cather, S.M., 1994. Introduction. In: Keller, G.R., Cather, S.M. (Eds.), *Basins of the Rio Grande Rift—Structure, Stratigraphy, and Tectonic Setting*. Geological Society of America Special Paper 291, pp. 1–3.
- Kendall, C., 1998. Isotope tracers in catchment hydrology. In: Kendall, C., McDonnell, J.J. (Eds.), *Elsevier Science B.V., Amsterdam*, pp. 519–576.
- Knöller, K., Trettin, R., Strauch, G., 2005. Sulphur cycling in the drinking water catchment area of Torgau–Mockritz (Germany): insights from hydrochemical and stable isotope investigations. *Hydrol. Process.* 19, 3445–3465.
- Kronfeld, J., 1974. Uranium deposition and Th-234 alpha-recoil: an explanation for extreme $^{234}\text{U}/^{238}\text{U}$ fractionation within the Trinity aquifer. *Earth Planet. Sci. Lett.* 21, 327–330.
- Kronfeld, J., Vogel, J.C., Talma, A.S., 1994. A new explanation for extreme $^{234}\text{U}/^{238}\text{U}$ disequilibrium in a dolomitic aquifer. *Earth Planet. Sci. Lett.* 123, 81–93.
- Krouse, H.R., Grinenko, V.A., 1991. *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment*. John Wiley & Sons.
- Krouse, H.R., Mayer, B., 2000. Sulphur and oxygen isotopes in sulphate. In: Cook, P., Herczeg, A.L. (Eds.), *Environmental Tracers in Subsurface Hydrology*. Kluwer Academic Publishers, pp. 195–231.
- Langford, R.P., 2003. The Holocene history of the White Sands dune field and influences on eolian deflation and playa lakes. *Quat. Int.* 104, 31–39.
- Langmuir, D., 1978. Uranium solution–mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta* 42, 547–569.
- Lueth, V.W., Rye, R.O., Peters, L., 2005. “Sour gas” hydrothermal jarosite: ancient to modern acid-sulfate mineralization in the southern Rio Grande Rift. *Chem. Geol.* 215, 339–360.
- Ma, L., Chabaux, F., Pelt, E., Blaes, E., Jin, L., Brantley, S., 2010. Regolith production rates calculated with uranium-series isotopes at Susquehanna/Shale Hills Critical Zone Observatory. *Earth Planet. Sci. Lett.* 297 (1–2), 211–225.

- Mallén, G., 2000. Isotopeanalytische charakterisierung hydrodynamischer und biogeochemischer Prozesse im Uferfiltrat und landseitigen Grundwässern der Torgauer Elbtalwanne unter besonderer Berücksichtigung der Herkunft und Umwandlungen von Kohlenstoff- und Schwefelspezies (Ph.D. thesis). UFZ Report 9/2000.
- Mayer, B., Fritz, P., Prietzel, J., Krouse, H.R., 1995. The use of stable sulfur and oxygen isotope ratios for interpreting the mobility of sulfate in aerobic forest soils. *Appl. Geochem.* 10, 161–173.
- Mees, F., 2003. Salt mineral distribution patterns in soils of the Otjomongwa pan, Namibia. *Catena* 54, 425–437.
- Mitchell, M.J., Krouse, H.R., Mayer, B., Stam, A.C., Zhang, Y., 1998. Use of stable isotopes in evaluating sulfur biogeochemistry of forest ecosystems. In: Kendall, C., McDonnell, J.J. (Eds.), *Catchment Hydrology*. Elsevier, Amsterdam, pp. 489–518.
- Mizota, C., Sasaki, A., 1996. Sulfur isotope composition of soils and fertilizers: differences between Northern and Southern hemispheres. *Geoderma* 71, 77–93.
- Moncaster, S.J., Bottrell, S.H., Tellam, J.H., Lloyd, J.W., Konhauser, K.O., 2000. Migration and attenuation of agrochemical pollutants: insights from isotopic analysis of groundwater sulfate. *Contam. Hydrol.* 43, 147–163.
- Moore, S.J., Bassett, R.L., Liu, B., Wolf, C.P., Doremus, D., 2008. Geochemical tracers to evaluate hydrogeologic controls on river salinization. *Ground Water* 46, 489–501.
- Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (version 2) – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water Resources Investigations Report, pp. 99–4259.
- Payero, J.O., Yonts, S.D., Irmak, S., Tarkalson, D., 2005. Advantages and disadvantages of subsurface drip irrigation. Extension of University of Nebraska Lincoln. EC776.
- Pelt, E., Chabaux, F., Innocent, C., Navarre-Sitchler, A.K., Sak, P.B., Brantley, S.L., 2008. Uranium–thorium chronometry of weathering rinds: rock alteration rate and paleo-isotopic record of weathering fluids. *Earth Planet. Sci. Lett.* 276 (1–2), 98–105.
- Phillips, F.M., Hogan, J.F., Mills, S.K., Hendrickx, J.M.H., Alsharhan, A.S., Wood, W.W., 2003. Environmental tracers applied to quantifying causes of salinity in arid-region rivers: results from the Rio Grande, southwestern USA. *Water Resources Perspectives: Evaluation, Management and Policy*. Elsevier Science, New York, pp. 327–334.
- Picchioni, G.A., Karaca, H., Boyse, L.G., McCaslin, B.D., Herrera, E.A., 2000. Salinity, boron, and irrigated pecan productivity along New Mexico's Rio Grande basin. *J. Environ. Qual.* 29, 955–963.
- Ragab, R., Prudhomme, C., 2002. Climate change and water resources management in arid and semi-arid regions: prospective and challenges for the 21st century. *Biosyst. Eng.* 81, 3–34.
- Rasouli, F., Pouya, A.K., Cheraghi, S.A.M., 2012. Hydrochemistry and water quality assessment of the Kor-Sivand Basin, Fars province. *Iran Environ. Monit. Assess.* 184, 4861–4877.
- Sevostianova, E., Leinauer, B., Sallenave, R., Karcher, D., Maier, B., 2011. Soil salinity and quality of sprinkler and drip irrigated warm-season turfgrasses. *Agron. J.* 103, 1773–1784.
- Shanley, J.B., Mayer, B., Mitchell, M.J., Michel, R.L., Bailey, S.W., Kendall, C., 2005. Tracing sources of streamwater sulfate during snowmelt using S and O isotope ratios of sulfate and ^{35}S activity. *Biogeochemistry* 76, 161–185.
- Sheta, A.S., Al-Sewailam, M.S., Sallam, A.Sh., Al-Mashhady, A.S., 2000. Nature and composition of newly formed precipitates in relationship to characteristics of groundwater in arid environment. *Arid Soil Res. Rehabil.* 14, 387–401.
- Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M., Bohlke, J.K., 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Anal. Chem.* 73, 4145–4153.
- Sims, K.W.W., Gill, J.B., Dosseto, A., Hoffmann, D.L., Lundstrom, C.C., Williams, R.W., Ball, L., Tollstrup, D., Turner, S., Prytulak, J., Glessner, J.G., Standish, J.J., Elliott, T., 2008. An inter-laboratory assessment of the thorium isotopic composition of synthetic and rock reference materials. *Geostandards and Geoanalytical Research* 32, 65–91.
- Simpson, C.R., Nelson, S.D., Melgar, J.C., Jifon, J., King, S.R., Schuster, G., Volder, A., 2014. Growth response of grafted and ungrafted citrus trees to saline irrigation. *Sci. Hortic.* 169, 199–205.
- Skrzypek, G., 2013. Normalization procedures and reference material selection in stable HCNOS isotope analyses – an overview. *Anal. Bioanal. Chem.* 405, 2815–2823.
- Skrzypek, G., Sadler, R., 2011. A strategy for selection of reference materials in stable oxygen isotope analyses of solid materials. *Rapid Commun. Mass Spectrom.* 25, 1625–1630.
- Szyrkiewicz, A., Witcher, J., Modelska, M., Borrok, D.B., Pratt, L.M., 2011. Anthropogenic sulfate loads in the Rio Grande, New Mexico. *Chem. Geol.* 283, 194–209.
- Szyrkiewicz, A., Borrok, D.M., Skrzypek, G., Rearick, M., 2015. Isotopic studies of the Upper and Middle Rio Grande. Part 1 – importance of sulfide weathering in the riverine sulfate budget. *Chem. Geol.* <http://dx.doi.org/10.1016/j.chemgeo.2015.05.022>.
- Trock, W.L., Huszar, P.C., Radosevich, G.E., Skogerboe, G.V., Vlachos, E.C., 1978. Socioeconomic and institutional factors in irrigation return flow quality control volume III: Middle Rio Grande Valley case study. Environmental Protection Agency (Report EPA-600/2-78-174c).
- U.S. Army Corps of Engineers, 2011. Alternative Analysis for the Rio Grande Salinity Management Program. (Prepared by CH2MHILL, <http://www.nmenv.state.nm.us/swqb/documents/swqbdocs/LRG/Program/RioGrandeSalinityAlternativesAnalysis09-26-11.pdf>).
- Van den Akker, J., Simmons, C.T., Hutson, J.L., 2011. Salinity effects from evaporation and transpiration under flood irrigation. *J. Irrig. Drain. Eng.* 137, 754–764.
- Victória, L., Otero, N., Soler, A., Canals, Á., 2004. Fertilizer characterization: isotopic data (N, S, O, C, and Sr). *Environ. Sci. Technol.* 38, 3254–3262.
- Wilcox, L.V., 1957. Analysis of salt balance and salt-burden data on the Rio Grande. In: Duisberg, P.C. (Ed.), *Problems of the Upper Rio Grande: An Arid Zone River: Socorro, New Mexico*. U.S. Commission for Arid Resource Improvement and Development, Publication no. 1, pp. 39–44.
- Williams, A.J., Crossey, L.J., Karlstrom, K.E., Newell, D., Person, M., Woolsey, E., 2013. Hydrogeochemistry of the Middle Rio Grande aquifer system – fluid mixing and salinization of the Rio Grande due to fault inputs. *Chem. Geol.* 351, 281–298.
- Witcher, J.C., King, J.P., Hawley, J.W., Kennedy, J.W., Williams, J., Cleary, M., Bothern, L.R., 2004. Sources of salinity in the Rio Grande and Mesilla Basin groundwater: New Mexico Water Resources Research Institute WRRRI Technical completion Report No. 330 168 p.
- Yuan, F., Miyamoto, S., 2005. Dominant process controlling water chemistry of the Pecos River in American southwest. *Geophys. Res. Lett.* 32, L17406. <http://dx.doi.org/10.1029/2005GL023359>.
- Yuan, F., Mayer, B., 2012. Chemical and isotopic evaluations of sulfur sources and cycling in the Pecos River, New Mexico. *U.S.A. Chem. Geol.* 291, 13–22.
- Yuan, F., Miyamoto, S., 2008. Characteristics of oxygen-18 and deuterium composition in waters from the Pecos River in American Southwest. *Chem. Geol.* 255, 220–230.
- Yuan, F., Miyamoto, S., Anand, S., 2007. Changes in major element hydrochemistry of the Pecos River in the American Southwest since 1935. *Appl. Geochem.* 22 (1978–1813).